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A METHOD FOR THE PROXIMATE ANALYSIS OF PLANTS.

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At the request of my friend and former instructor, Prof. Albert B. Prescott, of the University of Michigan, I have prepared the following scheme for the analysis of plants. This method will appear, in substance, in his new Proximate Organic Analysis, now nearly completed.

The plan submitted is the outgrowth of a quite varied experience in the proximate analysis of plants; no claim to originality is made, the sole aim being to arrange in one simple scheme those methods best suited to insure accuracy.

It must be premised that no one method is applicable in all cases, and that the operator will so modify and adapt the proposed processes as to best attain the truths he seeks. If the present scheme shall serve merely as an example, to be improved upon as discoveries multiply, it will at least have served to stimulate to the more thorough study, this side the Atlantic, of a much neglected, yet very important, branch of analysis. The American student, when first entering upon the study of plant analysis, is perplexed and disheartened, owing to the lack of any elementary treatise in which he

may find directions for the quantitative estimation of the various plant constituents. The works of Rochleder and Wittstein, while giving most valuable assistance in the investigation of special constituents and their separation from large quantities of the crude herb, still fail to give clear and practicable directions for the quantitative estimation of each constituent. Von Mueller's latest enlarged edition of Wittstein's Plant Analysis gives a scheme, most excellent in many respects, yet cumbered with tiresome methods of extraction and manipulation, which serve to unnecessarily lengthen the time required for making the analyses without increasing the accuracy of results obtained.

Too many American analyses of plants have been summarized thus: "The plant contains gum, resin, tannin, a volatile oil, and a peculiar bitter principle, to which may be ascribed its medicinal activity." The foreign journals bring occasionally most excellent examples of accurate examinations of vegetable substances; as instances may be cited the examination of ginger, by J. C. Thresh,* and of ergot,† aloes,‡ and other articles, by Prof. Dragendorff. To these sources the student must look for his best models, until a more thorough and systematic training is given American students in proximate organic analysis.

In following the plan now presented, the use of the apparatus for repercolation is strongly urged for the extractions with benzole, alcohol, and other volatile solvents. A very simple and inexpensive apparatus has been described by various American and foreign chemists.§

"In any convenient water-tight vessel is a worm of block tin pipe, having an internal diameter of 9 m. m., and a length of about 2.5 metres. The lower (external) part of this worm is fitted, by an ether-soaked, velvet cork, to a glass percolator having a diameter of 4 c. m., a length of 20 c. m. to the constriction, and 5 c. m. below. Within this percolator is a smaller tube, flanged at the top and bottom, and suspended by fine platinum or copper wires. This tube has a diameter of

* Phar. Jour. Trans. [3], 10, 81, Aug. 1879.

† Phar. Jour. Trans. [3], 6, 1001, June 17, 1876.

‡ Werthbestimmung, 1874, p. 110.

§ B. Tollens, Zeitsch. f. Anal. Chem. [17], 320, 1878; New Remedies, [7], 335, Nov. 1878; W. O. Attwater, Proc. Am. Chem. Soc. [2], 2, p. 85; S. W. Johnson, Am. Jour. Sci. Arts, [13], 196; H. B. Parsons, New Remedies, [8], 293, Oct. 1879.

2.5 to 2.8 c. m., and a length of 14 c. m.; the bottom is covered by filter paper and fine washed linen,* tied on by linen thread. The weighed sample of the finely powdered herb is placed within this tube for extraction. A light glass flask, weighing about thirty grams, is fitted by an ether-soaked cork to the outer percolator." Having introduced the solvent into this glass flask, the connections are made secure, and heat is applied, by a water-bath, to the flask. If the liquid is too slowly volatilized, the addition of a little common salt to the water in the bath serves to remove the trouble.

Next in importance is the use of a good tared filter. The form originally presented by F. A. Gooch† leaves little to be desired. It may be made by perforating with fine holes the bottom of an ordinary platinum crucible, and fitting it accurately to a perforation made in a large rubber cork; this cork connects it with a receiving vessel, which, in turn, is connected with a Bunsen's pump. Fine asbestus suspended in water is poured into the crucible, the air exhausted from the receiving vessel, and thus a firm thin layer of asbestus is deposited on the bottom of the crucible. After ignition and weighing, the crucible is ready for the reception of any precipitate which it is desired to separate and weigh.

The use of these two pieces of apparatus will eliminate two grave sources of error, viz., incomplete extraction of soluble matters, and inaccuracies introduced by the use of tared paper filters.

The other necessary apparatus is simple, and includes one or more platinum crucibles and evaporating dishes, accurate burettes and graduated cylinders, a good balance, sensitive to at least .5 milligram, and the ordinary glass and porcelain ware found in all laboratories.

It is assumed that whoever attempts the analysis of a plant is informed as to the normal constituents to be sought, that he has had considerable experience in inorganic analysis, and in the identification of the principal classes of proximate con-

* In place of the linen and filter paper may be substituted fine brass or platinum wire gauze. Asbestus suspended in water may then be poured in to form a fine felt. The tube can then be dried and weighed, and the amounts extracted may be found by the loss of weight of the tube and substance. A little experimentation will show the operator how to prepare and use the tube. It is but an adaptation of the Gooch's filter here recommended.

†Proc. Amer. Acad. Sci. [13], 342, 1878; New Remedies, [7], 290, Oct. 1878; This Journal, 1, 317.

stituents which he now undertakes to estimate quantitatively. Accordingly tests for identification will not be here presented; they should, however, never be omitted. The necessity of recording in detail all physical and chemical peculiarities, with every weight that is taken, is self-evident.

A Method for the Proximate Analysis of Plants.

I. *Preparation of Sample.*

The air-dry specimen should be carefully examined, and all extraneous substances removed. The entire sample should then be ground, or beaten in an iron mortar, until it will all pass through a sieve having from forty to sixty meshes to the linear inch. After thoroughly mixing this sample, take of it about one hundred grams, which should be further pulverized until it will all pass through a sieve having from eighty to one hundred meshes to the linear inch. From this smaller portion remove all iron, derived from mill or mortar, by use of a magnet. Then place in a clean dry bottle, which should be labelled and securely corked. This small sample is for the analysis; the larger portion should be reserved for the separation of those proximate principles which seem, from the analysis, to be worthy of more extended investigation.

II. *Estimation of Moisture.*

Dry rapidly, at 100 to 120°C., two or more grams of the sample; the loss of weight equals moisture, and occasionally a little volatile oil. In some cases it is best to dry at a lower temperature, and at other times the drying should be conducted in a stream of hydrogen or carbonic anhydride.

III. *Estimation of Ash.*

In a weighed crucible gently ignite two or more grams of the sample until nearly or quite free from carbonaceous matter; the heat should not be permitted to rise above faint redness, or loss of alkaline chlorides may occur. Weigh this residue as *crude ash*, and in it determine:

a. Amount soluble in Water.—This portion may contain chlorides, sulphates, phosphates, and carbonates of potassium and sodium, also slight amounts of chlorides and sulphates of calcium and magnesium.

b. Insoluble in Water; Soluble in dilute Hydrochloric Acid.—The residue from *a* should be treated with a slight excess of hydrochloric acid, and evaporated in a porcelain dish over a water-bath until all free acid has been expelled; it should then be again moistened with hydrochloric acid, water added, and be filtered from any remaining insoluble substances. This treatment removes carbonates (with decomposition) and phosphates of calcium and magnesium, sulphate of calcium, and oxides of iron and manganese.

c. Insoluble in Water; Insoluble in dilute Hydrochloric Acid; Soluble in concentrated Sodic Hydrate.—Boil the residue from *b* with a solution containing about twenty per cent. of sodic hydrate. This treatment removes combined silica of the ash. The residue still insoluble is sand and clay which adhered to the specimen; this residue should be separated, washed thoroughly, and weighed.

Always determine the amounts removed by the above treatment by weighing the dried, undissolved residues. The ash, as thus estimated, usually includes a little unconsumed carbon, together with more or less carbonic anhydride (CO_2), most, or all, of which was not originally present in the plant, but was produced by the combustion of the organic matter. For most purposes it is unnecessary to estimate and exclude from the ash this carbonic anhydride; where great accuracy is desired, a complete quantitative analysis should be made, the amount of each base and acid being determined, and in the statement of results only those should be included which existed originally in the plant. For this purpose it is necessary to burn from twenty to one hundred grams of the sample; for further directions consult text-books on agricultural and inorganic analysis.

IV. *Estimation of Total Nitrogen.*

In half a gram or more of the sample determine total nitrogen by combustion with excess of soda-lime, as directed by Prof. S. W. Johnson and E. H. Jenkins.* If later in the analysis no other nitrogenous substances are discovered, calculate the total amount of nitrogen to albuminoids by multiplying by 6.25. When other nitrogenous compounds are present, their

* Report Conn. Agric. Exp. Station, 1878; Chem. News, July 18, 1879, p. 28; This Journal, 1, p. 77.

content of nitrogen should be determined directly or by difference; after proper deductions have been made, the remaining nitrogen should be calculated to albuminoids.

V. *Estimation of Benzole Extract.*

In a suitable apparatus for repercolation completely exhaust 5 grams of the sample with pure coal-tar benzole (sp. gr. .85-.88, boils at 80-85° C, leaves no residue when evaporated). The extraction requires from four to six hours' continued action of the solvent. Carefully evaporate this liquid to dryness in a weighed dish, and record its weight as *total benzole extract*. This extract may contain volatile oils and other aromatic compounds, resins, camphors, volatile or non-volatile organic acids, wax, solid fats, fixed oils, chlorophyll, other colors, volatile or fixed alkaloids, glucosides, almost no ash.

To the weighed extract add water, again evaporate on the water-bath, and complete the drying in an air-bath at 110°C. In absence of other vaporizable substances the loss of weight approximates the amount of *volatile oil*. If the presence of a volatile alkaloid is suspected (from a characteristic odor or an alkaline reaction), add a drop of hydrochloric acid to prevent its volatilization. Camphors are partially dissipated by this treatment; hence, when they are present, this evaporation should be dispensed with.

Treat, now, the residue with a moderate amount of warm water, allow to stand until cool, then filter through fine paper by aid of a Bunsen's pump. In half of the aqueous filtrate determine *total organic matter* and *ash;* test the remaining half for *alkaloids, glucosides*, and *organic acids* by salts of lead, silver, barium and calcium. Care must be taken not to mistake a slight amount of suspended matter, frequently resinous, for other substances actually soluble in water.

The still undissolved residue should be again removed from filters and dishes by solution in benzole, the benzole solution being again evaporated to dryness. Treat this residue with warm, very dilute hydrochloric acid, allow to cool, and filter through paper. The filtrate should be tested for *alkaloids* and *glucosides*. The amount extracted by acid, if any, may be determined by weighing the still undissolved residue. Treat this residue with several considerable portions of eighty per

cent. alcohol (sp. gr. .8483 at 15.6°C.), allowing at least an hour for each treatment. Filter through paper and determine by evaporation the matter dissolved; this usually consists of *chlorophyll* with one or more *resins*, which may sometimes be separated by use of petroleum naphtha, chloroform, or similar solvents. Purified animal charcoal removes *chlorophyll* and *some resins* from alcoholic solution, while certain other resins are not removed. If *camphors* were present in the plant the greater portion will be found in the alcoholic liquid.

The substances undissolved by eighty per cent. alcohol may be *fixed oil*, *solid fat*, *wax*, and very rarely a *resin:* their separation may be attempted by refrigeration and pressure, or by use of ether, chloroform, etc.

Recapitulation.

1. Loss by evaporation, with precautions: *volatile oil.*
2. Soluble in water: *alkaloids, glucosides, organic acids.*
3. { Insoluble in water. / Soluble in dilute acids. } : *Alkaloids*, possibly *glucosides.*
4. { Insoluble in water. / Insoluble in dilute acids. } : *a.* { Removed by animal charcoal: *chlorophyll, some resins.* }
   { Soluble in 80 per cent. alcohol. } *b.* { Not removed by animal charcoal: *some resins.* }
5. { Insoluble in water. / Insoluble in dilute acids. / Insoluble in 80 per cent. alcohol. } : *wax, fats, fixed oils.*

It is frequently advantageous to extract the plant with petroleum naphtha (sp. gr. .66-.70, boils at about 50°C., wholly volatile) before treatment with benzole; by reference to the accompanying table of comparative solubilities it will be seen that this treatment may serve to separate fixed and volatile oils and some resins and colors, from certain solid fats, wax, other resins and colors.

Where benzole of sufficient purity cannot be had, pure chloroform is the best substitute. The use of ether is objectionable in this place, as its solvent properties are less distinctly marked than are those of naphtha, chloroform and benzole; in other words, more plant constituents are sparingly

TABLE OF COMPARATIVE SOLUBILITIES.

Substances.	Water.	Ab. Alcohol.	80 per ct. Alcohol.	Ab. Ether.	Chloroform.	Benzole.	Pet. Naph.	10 per ct. Ammonia.	Ammonic Cupric Oxide.	$H_2SO_4.H_2O$. Sp. gr. 1.78.	Fehling's Sol.	Lead Subacetate.
Volatile oils	Sp	Sol	Sol	Sol	Sol	Sol	Sol	Sol	....	....	.....	....
Fixed oils	Ins	Ins?	Ins	Sol	Sol	Sol	Sol	Sol?	....	....	.....	....
Wax	Ins	Sp	Sp	Sp	Sp	Sol	Sp?	Ins?	....	....	.....	....
Solid fats	Ins	Sp	Sp	Sp?	Sp?	Sol?	Sp?	Ins?	....	....	.....	....
Chlorophyll	Ins	Sol	Sol	Sol	Sol	Sol	Sp	Ins	....	....	.....	....
Soft resins	Ins	Sol	Sol	Sol	Sol	Sol	Sol	Ins?	....	....	.....	....
Hard resins	Ins	Sol?	Sol	Sol?	Sol?	Sol?	Sol?	Sol?	....	....	.....	....
Glucose	Sol	Ins	Sp	Ins	Ins	Ins	Ins	Sol	....	...	Reduced	Not prec
Sucrose	Sol	Ins	Sp	Ins	Ins	Ins	Ins	Sol	....	....	Not reduced†	Not prec
Tannin	Sol	Sol	Sol	Sp	Ins.	Ins	Ins	Sol	....	....	Reduced	Prec
Glucosides	Sol?	Sol?	Sol?	Sol?	Sol?	Sol?	Sol?	Sol?	....	....	Reduced†	Not prec
Alkaloids	Sol?	Sol?	Sol?	Sol?	Sol?	Sol?	Sol?	Sol?	....	....	.....	Not prec
Albuminoids	Sol?	Sol?	Sol?	Ins	Ins	Ins	Ins	Ins?	....	....	. ....	Prec
Gums	Sol	Ins	Ins	Ins	Ins	Ins	Ins	Sol?	....	....	Not reduced	Prec
Pectin	Sol	Ins	Ins	Ins	Ins	Ins	Ins	Sol?	....	....	.....	Prec
Pectic acid	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Sol	....	....	.....	Prec
Organic acids	Sol?	Sol?	Sol	Ins?	Ins?	Ins?	Ins?	Sol	....	...	.....	Prec?
Salts of org. acids	Sol?	Sol?	Sol?	Ins?	Ins?	Ins?	Ins?	Sol?	....	....	.....	Prec?
Starch	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	....	....	.....	....
Cellulose	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Sol	Sol	... ..	....
"Para cellulose"	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins*	Sol	.....	....
"Meta cellulose"	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Sol	.....	....
"Vasculose"	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	.....	....
"Extractives"	Sol*	Ins?	Sol?	Ins	Ins	Ins	Ins	Sol?	....	....	Reduced?	Not prec?
Colors	Sol?	Ins?	Sol?	Ins	Ins	Ins	Ins	Sol?	....	....	.....	Prec?

* "Para cellulose" soluble in ammonia-cupric oxide after boiling with dilute HCl.
† Glucosides reduce Fehling's solution after boiling with dilute acids; same with sucrose.
An ? shows that some marked variations or exceptions occur.
Sp — sparingly soluble. Sol — soluble. Ins — insoluble.

soluble in ether than in the above mentioned solvents. Consequently many substances which should properly be extracted by 80 per cent. alcohol, would be sparingly dissolved if ether were used, while benzole, chloroform, and naphtha would have no perceptible solvent action upon them; tannic acids may be cited as instances illustrating this point.

VI. *Estimation of Eighty per cent. Alcohol Extract.*

That part of the plant not dissolved by benzole should be dried at 100°C. and then completely exhausted by eighty per cent. alcohol (sp. gr. .8483 at 15.6°C.). This requires from twelve to fourteen hours' continuous treatment with the solvent. Remove, dry, and weigh any crystals or powder that may separate upon concentrating and cooling the alcoholic percolate. Make the clear liquid to a definite volume by adding more eighty per cent. alcohol. In an aliquot part of this liquid determine *total organic matter* and *ash:* in another equal portion determine *total organic matter* and *ash soluble in water,* and, by difference, *total organic matter insoluble in water.*

The remaining clear alcoholic liquid should be evaporated carefully to dryness, pulverized, and treated with several considerable portions of absolute alcohol (sp. gr. .7938 at 15.6°C.).

A. Soluble in Absolute Alcohol.

a. Soluble in water.

a^1. *Precipitated by subacetate of lead.*
Tannin and most organic acids; some extractives; some inorganic acids of the ash. Weigh in Gooch's filter, ignite cautiously, and again weigh; loss equals organic matter precipitated.

a^2. *Not precipitated by subacetate of lead.*
Alkaloids, glucosides, some extractives and colors. Determine by difference between *a* and *a*^{1}.

b. Insoluble in water.

b^1. *Soluble in dilute hydrochloric acid.*
Alkaloids, glucosides (rarely), some extractives. Determine by difference between *b* and *b*^{2}.

b^2. *Insoluble in dilute hydrochloric acid.*

b^1. *Soluble in dilute ammonic hydrate.*
Most acid resins, some colors. Determine by difference between b^2 and b^4.

b^4. *Insoluble in dilute ammonic hydrate.*
Neutral resins, some colors, albuminoids (in some seeds). Redissolve in alcohol, evaporate and weigh.

B. Insoluble in Absolute Alcohol.

c. Soluble in water.

c^1. *Precipitated by subacetate of lead.*
Some colors, extractives, albuminoids (rarely), organic acids, and inorganic acids of the ash. Weigh in Gooch's filter, ignite cautiously, and again weigh; loss equals organic matter precipitated.

c^2. *Not precipitated by subacetate of lead.*
Alkaloids, glucosides, sucrose, glucose, some extractives. Determine by difference between c and c^1. Remove Pb by H_2S, H_2SO_4, Na_2CO_3, or other means, and titrate for sucrose and glucose.

d. Insoluble in water.

d^1. *Soluble in dilute hydrochloric acid.*
Some alkaloids and glucosides. Determine by difference between d and d^2.

d^2. *Insoluble in dilute hydrochloric acid.*
Few resins, some extractives, and color substances. Dissolve in alcohol, evaporate and weigh in a tared dish.

In some cases it may be preferable to use the following method for analysis of the eighty per cent. alcohol extract; it is more desirable when the plant examined contains a considerable amount of sugars, tannic acid, etc.

Alcohol Extract, dilute to 200 c. c. with eighty per cent. alcohol.

1. In 20 c. c. determine *total organic matter* and *ash*.

2. In 20 c. c. determine *total organic matter* and *ash* that are *soluble in water*, and, by difference, *total organic matter insoluble in water*.

3. Evaporate the remaining 160 c. c. to dryness, treat with water, filter, and make the filtrate measure 160 c. c. Reserve the insoluble matter on the filter for examination. (10).

4. In 20 c. c. of the aqueous solution determine tannin gravimetrically by A. Carpeni's method;* precipitate by ammoniacal acetate of zinc, use a Gooch's filter, wash the precipitate with very weak ammonia, dry at 120°C., weigh, ignite cautiously, again weigh. The loss by ignition equals tannic acid, in absence of certain interfering substances.

5. Precipitate 20 c. c. by normal acetate of lead, and determine, as before described, the amount of organic matter after drying at 100–120°C. This precipitate will contain, if the substances are present in the plant, *tannic*, *gallic*, and most other *organic acids*, some *colors*, rarely *albuminous substances*, some *extractives*, and most *inorganic acids* of the ash. Determine, by difference, the amount not precipitated by this treatment.

6. In 20 c. c. determine in like manner the amount precipitated by basic acetate ("subacetate") of lead. This reagent precipitates a greater number of acids, colors and extractives than are precipitated by the normal acetate, hence it is frequently possible to estimate such substances by subtracting the amount precipitated by one reagent from the amount precipitated by the other. To the filtrate add a slight excess of dilute hydrochloric acid, boil gently for half an hour, and determine in the liquid *total glucose* by use of Fehling's solution.

7. Precipitate 20 c. c. by subacetate, exactly as in 6, and use the precipitate as a duplicate to check the amount there estimated. To the filtrate add a very slight excess of solution of carbonate of sodium, filter from the carbonate of lead, wash well with water containing a little alcohol, and in the filtrate estimate *actual glucose*. If the glucose thus found is appreciably less than that in 6, subtract it from that amount; this glucose may be due to the presence in the plant of *sucrose* or some *glucoside*. If due to sucrose, the amount of the latter may be found by multiplying this residual glucose by .95; if to a glucoside, a fit subject for an extended investigation is presented. The properties, formula, and decomposition products of the newly-found glucoside should be carefully studied.

8. Precipitate 20 c. c. with subacetate of lead, as in 6 and 7, employing the precipitate as material from which to separate

* Chem. News, July 9, 1875, p. 19, from Gaz. Chim. Ital. 1875, No. 3; Proc. Am. Ph. Assn. 1875, p. 341.

organic acids, after removal of lead by sulphuretted hydrogen. Acidulate the filtrate with sulphuric acid, add an equal volume of alcohol, allow to stand two hours, filter, wash the precipitate with fifty per cent. alcohol, and evaporate the filtrate until all alcohol has been dissipated. Test the acid solution for *alkaloids, glucosides, sugars, extractives.*

9. Reserve the remaining 40 c. c. for duplicating any unsatisfactory determinations.

10. The residue mentioned in 3 as insoluble in water may contain *resins, albuminoids* (especially from seeds), *colors, alkaloids, glucosides.* Dilute acids remove *alkaloids* and some *glucosides,* dilute ammonic hydrate will remove some *resins, colors,* and *glucosides.* Any still insoluble residue probably contains *albuminous* or *resinous* substances.

VII. *Estimation of Cold Water Extract.*

That part of the plant remaining insoluble after treatment with alcohol should be dried at 110°C. and completely extracted by cold water. When the plant contains considerable mucilaginous matter, this is best removed by placing the substance in a flask or graduated cylinder, and then adding a measured volume of cold water. Allow to macerate, with frequent agitation, for from six to twelve hours; then filter through fine washed linen, and evaporate an aliquot portion of the solution. In this residue determine *total organic matter* and *ash.* This residue usually contains little but *gum;* in analysis of fruits and fleshy roots *pectin bodies, salts of organic acids,* rarely a substance resembling *dextrin,* and small amounts of *albuminous substances* and *coloring matter.* Usually the separation of these substances is very difficult. The unevaporated liquid should be used for such qualitative reactions as are necessary to show the nature of the substances extracted. The insoluble residue should be well washed with water, transferred to a crucible, and completely dried at 110° C. This residue should be then weighed.

VIII. *Estimation of Acid Extracts.*

The dried residue insoluble in cold water should be transferred to a beaker containing 500 c. c. of water and 5 c. c. of

concentrated sulphuric acid (sp. gr. 1.84). Boil for six hours, on a gauze support, adding water to keep the volume of liquid unchanged; if the substance be very starchy, a longer boiling may be necessary. This treatment will convert *starch* and its *amorphous isomers* to dextro-glucose, and will occasionally remove some *salt of an organic acid*, with usually traces of *albuminous* and *indeterminate* substances.

The *total amount extracted* may be found by washing, drying at 110°C., and weighing the yet insoluble residue, and subtracting the weight from the one taken after extracting with cold water. The amount of *starch and isomers* may be found by determining in a given volume of the acid filtrate the amount of *glucose*, using Fehling's solution; the glucose thus found multiplied by .9 equals starch and isomers. The *total extract* minus *starch and isomers* equals *acid extract not starch.* This includes a small amount of *ash*, which may be approximately determined by evaporating and igniting a known volume of the solution.

Where it is wished to separate the extracted matter from the sulphuric acid, boil the liquid with an excess of powdered barium carbonate until no acid reaction remains. Filter, and evaporate to dryness. The residue consists chiefly of hydrated dextro-glucose ($C_6H_{12}O_6.H_2O$), with some ash.

IX. *Estimation of Alkali Extract.*

Wash well and dry at 110°C. the residue from treatment with acid, and record its weight. Boil this residue, for two hours, with 500 c.c. of a solution containing 20 grams of sodic hydrate to the litre. Filter through fine washed linen, and wash the residue thoroughly with hot water, alcohol and ether. Transfer it to a weighed crucible, dry at 110-120°C., and weigh the residue as *crude fibre* and *ash;* this weight subtracted from the previous one shows the *total alkali extract.* This extract is largely *albuminous matter* and various modifications of *pectic* acid, Fremy's "*cutose,*" and various *coloring, humus,* and *decomposition compounds* in small amounts. Most of the extracted substances may be precipitated by excess of an acid with or without the presence of alcohol.

X. *Cellulose.*

The crude fibre from IX should be treated with from 50 to 100 c.c. of U. S. P. solution of chlorinated soda and allowed to stand twenty-four hours. If not then bleached white, slightly acidulate with hydrochloric acid, and set aside for another day. Filter through fine linen, or Gooch's filter, wash with hot water, dry at 110-120°C., and weigh, ash free, as *cellulose*. The loss of weight by this treatment state as *lignose* and *color*.

Remarks.

It is advisable to determine always, in addition to what has already been directed, the amounts extracted directly from the sample by water, ether, alcohol of various percentages, methylic alcohol, naphtha, chloroform, carbon disulphide, etc. In each extract estimate *total organic matter* and *ash*, determine qualitatively, and quantitatively when possible, its constituents, by treating with such solvents and reagents as are indicated. Each extract being composed of certain distinct substances, it is necessary to account for them in every case.

The amounts present of some constituents may be found by subtracting the weight extracted by some one solvent from the weight extracted by some other. It will be seen that this is a method of limited applicability, which can only be applied in those cases where the difference between the solvent action of the two liquids is very sharply defined. Certain special methods for the estimation of single constituents may be used, care being taken that all interfering substances be first removed. The methods of preparation of known substances as given in Husemann's Pflanzenstoffe, and to a considerable extent in Watt's Dictionary, may serve as suggestions for work. Treatment with benzole, eighty per cent. alcohol, and water, removes from nearly all plants the constituents of greatest chemical and medicinal interest, but in analyses of grains, fodder, and food materials those compounds extracted by dilute acids and alkalies have great value. There are substances in plants, seemingly isomers of starch and cellulose, which have properties more or less resembling those of cellulose, and are changed by boiling with dilute acids to glucose. In absence of an established nomenclature it has seemed best

to use the terms "starch isomers," or "amylaceous cellulose" for these substances,* while those constituents, *not albuminous*, which are not removed by dilute alkali have been termed "alkali extract." These substances have been investigated by various chemists, but no definite and authoritative nomenclature has yet been adopted. Thomsen gives the name "holz-gummi",† *wood-gum*, to a white substance extracted from plants by dilute sodic hydrate, while Fremy regards these various compounds as modifications of pectic acid, pectin, and "cellulose bodies."‡ Starch also may exist in some seeds (as of sweet corn) in a form soluble in water.§

It will be seen that the field for investigation is limitless, and almost unoccupied as yet, and that there is great need for improved methods for proximate analysis. The analyst will find that a study of any common plant will require of him much more than unthinking, mechanical habits of manipulation, while every careful investigation will reveal to him some constituents deserving more full and accurate study.

WASHINGTON, D. C., *Nov. 26th*, 1879.

ON THE ESTIMATION OF PHOSPHORIC ACID AS MAGNESIC PYROPHOSPHATE.‖

BY F. A. GOOCH.

The investigation of which this paper is an account, was undertaken at the request of Dr. Wolcott Gibbs, for the purpose of finding, for use in his work upon the complex inorganic acids, the best mode of proceeding in determining the phosphoric oxide of phosphotungstates and phosphomolybdates by precipitation as ammonio-magnesic phosphate and estimation as magnesic pyrophosphate. During the course of

* U. S. Dept. of Agric. Report, 1878, p. 189.

† Kolbe's Jour. Prak. Chem. Band 19, p. 146.

‡ Compt. rend. lxxxiii. 1136; Jour. Ch. Soc. 1877, p. 229.

§ U. S. Dept. of Agric. Report, 1878, pp. 153–155.

‖ Presented to the American Academy of Arts and Sciences. Communicated by the Author.

the work it has been found necessary to review much of what has been previously published concerning this method of determining phosphoric acid.

In a paper upon this subject, Kubel* criticised Fresenius's correction† (subsequently withdrawn‡) for the solubility of ammonio-magnesic phosphate in water containing free ammonia and magnesia mixture, and asserted that such correction is not only unnecessary, but that the results of the analysis are of themselves much higher than theory indicates, unless the precipitate is, after washing, dissolved and reprecipitated. Kubel's method was to add hydrochloric acid and then ammonia, or ammonic chloride, or ammonia, to a measured amount of a solution of sodic phosphate, to precipitate with magnesic sulphate mixture, and after twelve hours to filter off and wash with dilute ammonia containing one part of strong ammonia to three of water. A number of analyses made in this way gave amounts of phosphoric oxide varying from 101.5 to 104.3 per cent. of the real quantity present,—the actual weight being in each case 0.1986 gr. Another set of analyses in which the precipitate was, after washing, dissolved in hydrochloric acid and again thrown down with ammonia, but which were otherwise treated in the same manner as the first, gave figures for phosphoric oxide varying from 99.8 per cent. to 100.5 per cent. of the real amount. When the precipitate was twice dissolved and twice reprecipitated, the amount of phosphoric oxide indicated was 99.8 per cent., and when three times dissolved and reprecipitated, 99.2 per cent. of the real amount. While noting that the precipitate is not absolutely insoluble in ammonia, more especially if it contain ammonic chloride, Kubel concludes, supposing that a basic sulphate or hydrate of magnesium is thrown down with the first precipitate, that this precipitate must be dissolved after washing and again thrown down with ammonia.

Kissel,§ by using large amounts of ammonic chloride, washing copiously in order to make the solubility of the precipitate compensate for the inclusion of foreign matter, and taking care to use no great excess of the magnesic sulphate mixture, obtains in one set of experiments from 99.4 to 99.6

* Zeitschrift f. anal. Chem. VIII. 125.
† Anleitung zur Quant. Anal. 5 Aufl. 333.
‡ Ibid. 6 Aufl. 184.
§ Zeitschrift f. anal. Chem. VIII. 169.

per cent., in another from 99.8 to 100 per cent., of the correct amount of phosphoric oxide. Of three filtrates from the precipitated ammonio-magnesic phosphate, two gave weak reactions for phosphoric acid with acid ammonic molybdate, and one no reaction. The wash-water tested by the same method gave in every case a plain reaction. Heintz* supports Kubel so far as to say that in presence of any considerable excess of magnesic sulphate mixture the precipitate must be dissolved after incomplete washing. Brunner† points out that the solution must not be precipitated hot by magnesic sulphate mixture on account of the danger of throwing down magnesic hydrate. Schumann‡ supports Kissel in the view that the solution of the first precipitate is unnecessary, but adds a caution against the addition of ammonia after the magnesic sulphate mixture.

Finally, Abesser, Jani, and Mærcker§ substantiate Kubel's results, and having proved the presence of a sulphate in the precipitate, obtain somewhat better figures by igniting over the blast. Adopting the method of precipitating by magnesic chloride mixture previously suggested by Brassier‖ and Bunsen,¶ and recommended in the works of Rose** and Fresenius,†† their analyses show from 99.96 per cent. to 100.48 per cent. of the true amount of phosphoric oxide. The weight of phosphoric oxide used in each of their experiments was not far from 0.1250 gr. The precipitate was washed until the reaction for chlorine with argentic nitrate failed to appear in the filtrate acidified with nitric acid. The method of precipitating with magnesic chloride and igniting over the Bunsen lamp, gave in their hands from 99.96 to 100.48 per cent.; the method of precipitating with magnesic sulphate and igniting over the blast, from 100.4 to 100.7 per cent.; and the method of precipitating with magnesic sulphate and igniting over the Bunsen lamp, from 101.4 to 103.1 per cent. of the actual amount of phosphoric oxide.

All agree that the precipitated ammonio-magnesic phosphate is soluble to a very considerable extent in dilute ammonia, and to a greater extent in ammonia containing ammonic

* Zeitsch. f. anal. Chem. IX. 16. † Ibid. XI. 30. ‡ Ibid. XI. 382. § Ibid. XII. 239.
‖ Ann. de Chim. et de Phys. [4] VII. 335. ¶ Zeitschrift f. anal. Chem. X. 405.
** Rose's analytische Chemie, VI. Aufl., 512, bearbeitet von Finkener.
†† Anleit. zur Quant. Anal., 6 Aufl., 403.

chloride; that the presence of a magnesia salt tends to prevent the solution of the precipitate; and that when magnesic sulphate is used in excess as a precipitant, the precipitate includes, mechanically or otherwise, an appreciable amount of magnesic sulphate, or magnesic hydrate, or both. Kissel and Schumann aim to arrive at correct results by precipitating with as little excess of magnesic sulphate mixture as possible, and compensating for foreign inclusions by dissolving a part of the precipitate. Kubel and Heintz strive to reach the same end by removing the excess of the precipitant, together with the included impurity, by filtering off, dissolving, and again throwing down the precipitate.

With this preface, I proceed to the description of my own experiments upon this subject.

I have worked with measured portions of solutions of hydro-disodic phosphate, or of microcosmic salt, the standards of which were, in all cases but one, determined by evaporating a known volume to dryness, igniting the residue and weighing the remaining sodic pyrophosphate or metaphosphate as the case might be. In the one exceptional case, a known weight of microcosmic salt, freshly crystallized and dried, the volatile constituents of which had been determined by igniting separate portions, was dissolved in a known volume of water. The experiments which fixed the standards of these solutions are given below.

I. Two portions of 20 cm.³ each of a solution of hydro-disodic phosphate were evaporated to dryness, and the residue was ignited and weighed as sodic pyrophosphate.

(1) gave of $Na_4P_2O_7$ 0.1217 gr.
(2) " " 0.1214 gr.

The solution contained, therefore, 0.1298 gr. of P_2O_5 to every 40 cm.³

II. A quantity of microcosmic salt was recrystallized, dried between papers by pressure, and the amount of loss on ignition determined in two portions.

(1) 1.1419 gr. gave of $NaPO_3$ 0.5836 gr. = 51.11 per ct.
(2) 0.9846 gr. " " 0.5027 gr. = 51.06 per ct.

Of this salt 3.7583 gr. were dissolved in water and the solution diluted to one litre. The solution contained, therefore, 0.0512 gr. of P_2O_5 to every 40 cm.³

III. The solution contained hydro-disodic phosphate.

(1) gave $Na_4P_2O_7$ from 40 cm.^{3} 0.3490 gr.

(2) " " " " 0.3490 gr.

Every 40 cm.^{3} contained, therefore, 0.1863 gr. P_2O_5.

IV. The solution contained hydro-disodic phosphate.

(1) gave $Na_4P_2O_7$ from 40 cm.^{3} 0.3530 gr.

(2) " " " " 0.3533 gr.

Every 40 cm.^{3} contained, therefore, 0.1885 gr. P_2O_5.

V. The solution contained hydro-disodic phosphate.

(1) gave $Na_4P_2O_7$ from 40 cm.^{3} 0.3512 gr.

(2) " " " " 0.3514 gr.

Every 40 cm.^{3} contained, therefore, 0.1875 gr. P_2O_5.

VI. The solution contained hydro-disodic phosphate.

(1) gave $Na_4P_2O_7$ from 40 cm.^{3} 0.4112 gr.

(2) " " " " 0.4113 gr.

Every 40 cm.^{3} contained, therefore, 0.2195 gr. P_2O_5.

VII. The solution contained hydro-disodic phosphate.

(1) gave $Na_4P_2O_7$ from 40 cm.^{3} 0.3429 gr.

(2) " " " " 0.3429 gr.

Every 40 cm.^{3} contained, therefore, 0.1831 gr. P_2O_5.

VIII. The solution contained microcosmic salt.

(1) gave $NaPO_3$ from 40 cm.^{3} 0.3077 gr.

(2) " " " " 0.3078 gr.

Every 40 cm.^{3}, therefore, contained 0.2142 P_2O_5.

IX. The solution contained microcosmic salt.

(1) gave $NaPO_3$ from 40 cm.^{3} 0.2897 gr.

(2) " " " " 0.2900 gr.

Every 40 cm.^{3} contained, therefore, 0.2017 gr. P_2O_5.

X. The solution contained hydro-disodic phosphate.

(1) gave $Na_4P_2O_7$ from 20 cm.^{3} 0.0247 gr.

(2) " " " " 0.0249 gr.

Every 40 cm.^{3} contained, therefore, 0.0265 gr. P_2O_5.

XI. The solution contained hydro-disodic phosphate.

(1) gave $Na_4P_2O_7$ from 20 cm.^{3} 0.0249 gr.

(2) " " " " 0.0250 gr.

Every 40 cm.^{3} contained, therefore, 0.0266 gr. P_2O_5.

XII. The solution consisted of 71.5 cm.^{3} of Solution IV. diluted to 500 cm.^{3} Every 40 cm.^{3} contained, therefore, 0.0270 gr. P_2O_5.

XIII. The solution consisted of 71.5 cm.^{3} of Solution IV.

diluted to 500 cm.³ Every 40 cm.³ contained, therefore, 0.0270 gr. P_2O_5.

XIV. The solution consisted of 61.3 cm.³ of Solution VI. diluted to 500 cm.³ Every 40 cm.³ contained, therefore, 0.0269 gr. P_2O_5.

XV. The solution consisted of 61.3 cm.³ of Solution VI. diluted to 500 cm.³ Every 40 cm.³ contained, therefore, 0.0269 gr. P_2O_5.

XVI. The solution consisted of 125.6 cm.³ of Solution VIII. diluted to one litre. Every 40 cm.³ contained, therefore, 0.0269 gr. P_2O_5.

Each of the following experiments was made with 40 cm.³ of another of these solutions diluted (if necessary), so that the volume after precipitation should for the weaker solutions be about 100 cm.³, and for the stronger solutions from 125 cm.³ to 150 cm.³

Precipitation was effected in cold solutions unless the contrary is stated, and, when not otherwise specified, either by a magnesic sulphate mixture consisting of one part of crystallized magnesic sulphate, two of ammonic chloride, four of concentrated ammonia, and eight of water; or by a magnesic chloride mixture containing three parts of crystallized magnesic chloride, eight of ammonic chloride, sixteen of concentrated ammonia, and thirty-two of water. The precipitate of ammonio-magnesic phosphate was, in every case, finally collected on asbestus felt in a perforated platinum crucible according to the process previously described by me,* washed with 60 cm.³ to 70 cm.³ (applied in successive portions) of a solution of one part of concentrated ammonia to three of water,— this amount being found to be more than sufficient for washing, when the asbestus process is used, until the filtrate ceases to show the presence of chlorine when treated with nitric acid and argentic nitrate,—moistened with a few drops of a solution of ammonic nitrate in ammonia, dried on the vacuum pump, ignited on a platinum crucible-cover, at first gently until fumes of ammonic nitrate no longer appeared, then at a full red heat until the spreading of a glow over the whole residue indicated the formation of the magnesic pyrophosphate.

* Proceedings Amer. Acad. Arts and Sci. XIII. 342; and This Journal, 1, 317.

The results of the experiments are tabulated below. The figures of the first column show the weights of magnesic pyrophosphate found, those of the second the corresponding weights of phosphoric oxide, those of the third the weight of phosphoric oxide required by the determinations of the standard of the solution used, those of the fourth the absolute error in the determination of phosphoric oxide, and those of the fifth the percentage error referred to the actual amount of phosphoric oxide present. The Roman numeral standing against the record of each experiment shows which phosphate solution was used in that experiment.

Alkaline Phosphates.

Experiments (1) to (10) inclusive were made with 40 cm.³ each of the phosphate solution. Portions (1) and (2) were precipitated with 20 cm.³ of magnesic sulphate mixture. Portions (3) to (6) were treated with 20 cm.³ of a magnesic sulphate mixture containing only a small amount of free ammonia, but the same weights of magnesium and ammonium salts as the regular mixture. The first precipitates of (3) and (4) were dissolved in hydrochloric acid and again thrown down by ammonia in presence of the excess of the precipitant, and those of (5) and (6) were dissolved and reprecipitated in this manner twice. Portions (7) to (10) were precipitated with 20 cm.³ of magnesic sulphate mixture after being acidulated—(7) and (8) with hydrochloric acid, (9) and (10) with 0.5 gr. of citric acid—and made alkaline with ammonia.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
I.	(1)	0.2082 gr.	0.1331 gr.	0.1298 gr.	+ 0.0033 gr.	+ 2.54
	(2)	0.2113 gr.	0.1352 gr.	0.1298 gr.	+ 0.0054 gr.	+ 4.16
	(3)	0.2104 gr.	0.1346 gr.	0.1298 gr.	+ 0.0048 gr.	+ 3.70
	(4)	0.2124 gr.	0.1358 gr.	0.1298 gr.	+ 0.0060 gr.	+ 4.62
	(5)	0.2095 gr.	0.1340 gr.	0.1298 gr.	+ 0.0042 gr.	+ 3.23
	(6)	0.2097 gr.	0.1342 gr.	0.1298 gr.	+ 0.0044 gr.	+ 3.39
X.	(7)	0.0420 gr.	0.0269 gr.	0.0265 gr.	+ 0.0004 gr.	+ 1.51
	(8)	0.0427 gr.	0.0273 gr.	0.0265 gr.	+ 0.0008 gr.	+ 3.02
	(9)	0.0444 gr.	0.0284 gr.	0.0265 gr.	+ 0.0019 gr.	+ 7.17
	(10)	0.0448 gr.	0.0286 gr.	0.0265 gr.	+ 0.0021 gr.	+ 7.92

Experiments (11) to (16) inclusive were made with portions of 40 cm.³ each of Solution II. Portions (11) and (12) were acidulated with hydrochloric acid and, after the addition of ammonia in excess, precipitated with 6 cm.³ of magnesic sulphate mixture. Portions (13) and (14) were acidulated with 0.5 gr. of citric acid and, after the addition of ammonia, treated with 6 cm.³ of magnesic sulphate mixture; which amount failing (on account of the presence of a citrate) to throw the phosphoric acid down entirely, 6 cm.³ more of the same mixture were added to complete the precipitation. Portions (15) and (16) were acidulated with hydrochloric acid and 0.5 gr. of citric acid, ammonia added in excess and precipitation effected with 12 cm.³ of magnesic sulphate mixture. The precipitates of (11), (13), and (15) were filtered off, washed and ignited; those of (12), (14), and (16) were filtered off on paper, drained, dissolved (without previous washing) in hydrochloric acid, thrown down again with ammonia, and, the precipitate having settled, filtered off, after the addition of a few centimetrs of magnesic sulphate mixture, upon asbestus, washed and ignited. The precipitates were all thrown down the first time from hot solutions.

	$Mg_2P_2O_7$	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
II.	(11) 0.0811 gr.	0.0519 gr.	0.0512 gr.	+ 0.0007 gr.	+ 1.37
	(12) 0.0801 gr.	0.0512 gr.	0.0512 gr.	0.	0.
	(13) 0.0827 gr.	0.0529 gr.	0.0512 gr.	+ 0.0017 gr.	+ 3.31
	(14) 0.0801 gr.	0.0512 gr.	0.0512 gr.	0.	0.
	(15) 0.0827 gr.	0.0529 gr.	0.0512 gr.	+ 0.0017 gr.	+ 3.31
	(16) 0.0801 gr.	0.0512 gr.	0.0512 gr.	0.	0.

Experiments (17) to (20) inclusive were made with portions of 40 cm.³ each of Solution III. To each portion were added 6 cm.³ of strong hydrochloric acid, 20 cm.³ of strong ammonia, and 20 cm.³ of magnesic sulphate mixture. The first precipitate was filtered off on paper, drained, dissolved in hydrochloric acid and thrown down again with ammonia. In portions (17) and (18) the second precipitation was effected instantly by adding concentrated ammonia to the acid solution, the precipitate being consequently quite voluminous, and magnesic sulphate mixture was added after settling. In portions (19) and (20) the second precipitation was brought about more gradually by neutralizing with dilute ammonia.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
III.	(17)	0.2928 gr.	0.1873 gr.	0.1863 gr.	+ 0.0010 gr.	+ 0.54
	(18)	0.2937 gr.	0.1878 gr.	0.1863 gr.	+ 0.0015 gr.	+ 0.80
	(19)	0.2923 gr.	0.1869 gr.	0 1863 gr.	+ 0.0006 gr.	+ 0.32
	(20)	0.2925 gr.	0.1871 gr.	0.1863 gr.	+ 0.0008 gr.	+ 0.43

In experiments (21) to (26) inclusive, 40 cm.³ of magnesic sulphate mixture, from which the ammonia had been removed by boiling, were in each case added to 40 cm.³ of the phosphate solution; in (21), (22), (23), and (24) directly, in (25) and (26) after acidifying with 5 cm.³ of strong hydrochloric acid and then making faintly but distinctly ammoniacal. In every case dilute ammonia was added gradually at first, and 5 cm.³ of strong ammonia after, the settling of the precipitate. Portions (21) and (22) were precipitated hot.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
V.	(21)	0.3112 gr.	0.1991 gr.	0.1875 gr.	+ 0.0116 gr.	+ 6.18
	(22)	0 3114 gr.	0.1992 gr.	0.1875 gr.	+ 0.0117 gr.	+ 6.24
	(23)	0.3028 gr.	0 1936 gr.	0.1875 gr.	+ 0.0061 gr.	+ 3.25
	(24)	0.3048 gr.	0.1949 gr.	0.1875 gr.	+ 0 0074 gr.	+ 3.94
VIII.	(25)	0 3469 gr.	0.3219 gr.	0 2142 gr.	+ 0.0077 gr.	+ 3.59
	(26)	0 3514 gr.	0 2248 gr.	0 2142 gr.	+ 0.0106 gr.	+ 4.94

For experiments (27) to (39) inclusive portions of 40 cm.³ each of the phosphate solutions were taken. To portions (27) and (28) were added 12 cm.³ of magnesic chloride mixture; to (29) and (30) 5 cm.³ of strong hydrochloric acid, strong ammonia to neutralization and 10 cm.³ beside, and then 12 cm.³ of magnesic chloride mixture; to portions (31) to (39) inclusive 5 cm.³ of strong hydrochloric acid, 20 cm.³ of strong ammonia and 10 cm.³ of magnesic chloride mixture, 5 cm.³ more of the same being added, except in experiment (31), after the settling of the precipitate.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
VI.	(27)	0.3430 gr.	0.2194 gr.	0 2195 gr.	— 0.0001 gr.	— 0.04
	(28)	0.3438 gr.	0.2199 gr.	0.2195 gr.	+ 0.0004 gr.	+ 0.18
	(29)	0.3425 gr.	0.2191 gr.	0.2195 gr.	— 0.0004 gr.	— 0.18
	(30)	0.3435 gr.	0.2197 gr.	0.2195 gr.	+ 0.0002 gr.	+ 0.09

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
III.	(31)	0.2902 gr.	0.1857 gr.	0.1863 gr.	— 0.0006 gr.	— 0.32
	(32)	0.2903 gr.	0.1857 gr.	0.1863 gr.	— 0.0006 gr.	— 0.32
	(33)	0.2908 gr.	0.1860 gr.	0.1863 gr.	— 0.0003 gr.	— 0.16
	(34)	0.2913 gr.	0.1863 gr.	0.1863 gr.	0.	0.
	(35)	0.2919 gr.	0.1866 gr.	0.1863 gr.	+ 0.0003 gr.	+ 0.16
	(36)	0.2920 gr.	0.1867 gr.	0.1863 gr.	+ 0.0004 gr.	+ 0.21
	(37)	0.2920 gr.	0.1867 gr.	0.1863 gr.	+ 0.0004 gr.	+ 0.21
IV.	(38)	0.2935 gr.	0.1877 gr.	0.1885 gr.	— 0.0008 gr.	— 0.42
	(39)	0.2941 gr.	0.1880 gr.	0.1885 gr.	— 0.0005 gr.	— 0.27

In experiments (40) to (43) inclusive 10 cm.³ of strong ammonia were added to 40 cm.³ of the phosphate solution and then 10 cm.³ of magnesic chloride mixture. The precipitates of (42) and (43) were dissolved by adding hydrochloric acid to the supernatant liquid and thrown down again with ammonia.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
V.	(40)	0.2946 gr.	0.1884 gr.	0.1875 gr.	+ 0.0009 gr.	+ 0.48
	(41)	0.2950 gr.	0.1887 gr.	0.1875 gr.	+ 0.0012 gr.	+ 0.64
	(42)	0.2927 gr.	0.1872 gr.	0.1875 gr.	— 0.0003 gr.	— 0.16
	(43)	0.2936 gr.	0.1878 gr.	0.1875 gr.	+ 0.0003 gr.	+ 0.16

In experiments (44) to (47) inclusive 10 cm.³ of strong ammonia were added to 40 cm.³ of the phosphate solution, and then 25 cm.³ of magnesic chloride. The precipitates of (46) and (47) were dissolved by hydrochloric acid added to the supernatant liquid and again thrown down with ammonia.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
IV.	(44)	0.2977 gr.	0.1904 gr.	0.1885 gr.	+ 0.0019 gr.	+ 1.01
	(45)	0.2986 gr.	0.1910 gr.	0.1885 gr.	+ 0.0025 gr.	+ 1.33
	(46)	0.2952 gr.	0.1888 gr.	0.1885 gr.	+ 0.0003 gr.	+ 0.16
	(47)	0.2954 gr.	0.1889 gr.	0.1885 gr.	+ 0.0004 gr.	+ 0.21

For each of the experiments (48) to (60) inclusive 40 cm.³ of the phosphate solution were taken. Portions (48), (49), (50) and (51) were precipitated with 40 cm.³ of magnesic chloride mixture containing 4 gr. of ammonic chloride more than the usual amount, the precipitant being added to the phosphate in experiments (48) and (49), the phosphate (gradually) to the precipitant in (50) and (51). In experiments (52) and (53) the solution of the phosphate was acidulated with 8 cm.³ of

hydrochloric acid, made alkaline with ammonia — about 4 gr. of ammonic chloride being produced in the process — and precipitated with 40 cm.³ of magnesic chloride mixture. In experiments (54) to (60) inclusive 40 cm.³ of magnesic chloride mixture from which the ammonia had been expelled by boiling were added to the phosphate solution — in experiments (56), (57), (58), (59) and (60) directly, in (54) and (55) after adding enough ammonia to make the solution smell distinctly of it — and ammonia afterward strong in (57), (58), (59) and (60), but dilute at first in (54), (55), and (56) and strong after the settling of the precipitate. Solutions (59) and (60) were precipitated hot.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
VII.	(48)	0.2880 gr.	0.1842 gr.	0.1831 gr.	+ 0.0011 gr.	+ 0.60
	(49)	0.2881 gr.	0.1843 gr.	0.1831 gr.	+ 0.0012 gr.	+ 0.66
	(50)	0.2886 gr.	0.1846 gr.	0.1831 gr.	+ 0.0015 gr.	+ 0.82
	(51)	0.2888 gr.	0.1847 gr.	0.1831 gr.	+ 0.0016 gr.	+ 0.87
	(52)	0.2882 gr.	0.1844 gr.	0.1831 gr.	+ 0.0013 gr.	+ 0.71
	(53)	0.2882 gr.	0.1844 gr.	0.1831 gr.	+ 0.0013 gr.	+ 0.71
	(54)	0.2865 gr.	0.1832 gr.	0.1831 gr.	+ 0.0001 gr.	+ 0.05
	(55)	0.2870 gr.	0.1835 gr.	0.1831 gr.	+ 0.0004 gr.	+ 0.22
V.	(56)	0.2931 gr.	0.1875 gr.	0.1875 gr.	0.	0.
	(57)	0.2940 gr.	0.1880 gr.	0.1875 gr.	+ 0.0005 gr.	+ 0.27
	(58)	0.2950 gr.	0.1887 gr.	0.1875 gr.	+ 0.0012 gr.	+ 0.64
	(59)	0.2983 gr.	0.1907 gr.	0.1875 gr.	+ 0.0032 gr.	+ 1.70
	(60)	0.3017 gr.	0.1930 gr.	0.1875 gr.	+ 0.0055 gr.	+ 2.93

In experiments (61) to (66) inclusive 5 cm.³ of strong hydrochloric acid were added to 40 cm.³ of the phosphate solution, and then ammonia in slight excess. Portions (61), (62), (63), and (64), were precipitated with 20 cm.³ of magnesic chloride mixture. To (65) and (66) were added 20 cm.³ of magnesic chloride mixture from which the ammonia had been expelled, and afterward ammonia dilute at the first and strong after the precipitate had settled. Solutions (63), (64), (65) and (66) contained previous to precipitating 3 gr. of sodic chloride each.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
XVI.	(61)	0.0426 gr.	0.0272 gr.	0.0269 gr.	+ 0.0003 gr.	+ 1.11
	(62)	0.0427 gr.	0.0273 gr.	0.0269 gr.	+ 0.0004 gr.	+ 1.49
	(63)	0.0430 gr.	0.0275 gr.	0.0269 gr.	+ 0.0006 gr.	+ 2.23
	(64)	0.0431 gr.	0.0276 gr.	0.0269 gr.	+ 0.0007 gr.	+ 2.60
	(65)	0.0426 gr.	0.0272 gr.	0.0269 gr.	+ 0.0003 gr.	+ 1.11
	(66)	0.0426 gr.	0.0272 gr.	0.0269 gr.	+ 0.0003 gr.	+ 1.11

Phosphotungstates.

In each of the following experiments upon the determination of phosphoric oxide in phosphotungstates 1 gr. of crystallized normal sodic tungstate ($Na_2WO_4.2H_2O$) was dissolved and added to 40 cm.^{3} of a phosphate solution, the phosphotungstate produced by the addition of acid in measured amount or until the yellow color of the solution indicated its formation, and ammonia added until the precipitate first formed redissolved.

In experiments (67) to (76) inclusive there were added to each portion containing the phosphate and tungstate 0.5 gr. of citric acid, hydrochloric acid, until the solution became yellow, ammonia until it gave its odor distinctly to the solution, and then 20 cm.^{3} of magnesic sulphate mixture. Portions (75) to (79) inclusive were treated in a similar manner, excepting that 5 cm.^{3} of strong hydrochloric acid and no citric acid were added to them. The precipitates of (67), (68), (69) and (70) were filtered off on asbestus, washed, and ignited in the manner previously described. The precipitates of (71), (72), (73) and (74) were filtered off on paper, washed with magnesic sulphate mixture, and then with a few centimeters of ammonia, dissolved in hydrochloric acid and reprecipitated with ammonia, a few centimeters of magnesic sulphate mixture being added after the precipitate had settled. The precipitates of (75) to (79) inclusive were filtered off on paper, washed with magnesic sulphate mixture, dissolved in hydrochloric acid and thrown down again with ammonia, a few centimeters of magnesic sulphate being added after the settling of the precipitate. The second precipitates were filtered off on asbestus, washed and ignited as usual.

		$Mg_2P_2O_7$	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
X.	(67)	0.0439 gr.	0.0281 gr.	0.0265 gr.	+ 0.0016 gr.	+ 6.04
	(68)	0.0445 gr.	0.0285 gr.	0.0265 gr.	+ 0.0020 gr.	+ 7.55
	(69)	0.0448 gr.	0.0286 gr.	0.0265 gr.	+ 0.0021 gr.	+ 7.92
	(70)	0.0455 gr.	0.0291 gr.	0.0265 gr.	+ 0.0026 gr.	+ 9.81
	(71)	0.0388 gr.	0.0248 gr.	0.0265 gr.	— 0.0017 gr.	— 6.41
	(72)	0.0390 gr.	0.0249 gr.	0.0265 gr.	— 0.0016 gr.	— 6.04
	(73)	0.0391 gr.	0.0250 gr.	0.0265 gr.	— 0.0015 gr.	— 5.66
	(74)	0.0394 gr.	0.0252 gr.	0.0265 gr	— 0.0013 gr.	— 4.90
	(75)	0.0421 gr.	0.0269 gr.	0.0265 gr.	+ 0.0004 gr.	+ 1.51
	(76)	0.0426 gr.	0.0272 gr.	0.0265 gr.	+ 0.0007 gr.	+ 2.64

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
XIII.	(77)	0.0424 gr.	0.0271 gr.	0.0270 gr.	+ 0.0001 gr.	+ 0.37
	(78)	0.0427 gr.	0.0273 gr.	0.0270 gr.	+ 0.0003 gr.	+ 1.11
	(79)	0.0428 gr.	0.0274 gr.	0.0270 gr.	+ 0.0004 gr.	+ 1.48

In experiments (80) to (82) and (85) to (88) inclusive there were added to each portion containing the phosphate and tungstate 0.5 gr. of citric acid, hydrochloric acid until the solution became yellow, ammonia in excess and 20 cm.³ of magnesic chloride mixture; in experiments (83) and (84), and (89) to (91) inclusive, 5 cm.³ of strong hydrochloric acid, with no citric acid, ammonia in excess and 20 cm.³ of magnesic chloride mixture. The precipitates of (85) to (91) inclusive were filtered off on paper, washed with magnesic chloride mixture, dissolved in hydrochloric acid and thrown down again with ammonia. The first precipitates of experiments (80) to (84) and the second precipitates of portions (85) to (91) were collected on asbestus, washed and ignited as usual.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
XI.	(80)	0.0454 gr.	0.0290 gr.	0.0266 gr.	+ 0.0024 gr.	+ 9.02
	(81)	0.0464 gr.	0.0297 gr.	0.0266 gr.	+ 0.0031 gr.	+ 11.65
	(82)	0.0466 gr.	0.0298 gr.	0.0266 gr.	+ 0.0032 gr.	+ 12.03
XVI.	(83)	0.0444 gr.	0.0284 gr.	0.0269 gr.	+ 0.0015 gr.	+ 5.58
	(84)	0.0447 gr.	0.0286 gr.	0.0269 gr.	+ 0.0017 gr.	+ 6.32
XII.	(85)	0.0405 gr.	0.0256 gr.	0.0270 gr.	− 0.0014 gr.	− 5.18
	(86)	0.0414 gr.	0.0265 gr.	0.0270 gr.	− 0.0005 gr.	− 1.85
	(87)	0.0414 gr.	0.0265 gr.	0.0270 gr.	− 0.0005 gr.	− 1.85
	(88)	0.0416 gr.	0.0266 gr.	0.0270 gr.	− 0.0004 gr.	− 1.48
XIII.	(89)	0.0423 gr.	0.0270 gr.	0.0270 gr.	+ 0.	0.
	(90)	0.0424 gr.	0.0271 gr.	0.0270 gr.	+ 0.0001 gr.	+ 0.37
	(91)	0.0430 gr.	0.0275 gr.	0.0270 gr.	+ 0.0005 gr.	+ 1.85

In experiments (92) to (101) inclusive 5 cm.³ of strong hydrochloric acid were added to each portion containing the phosphate and tungstate, ammonia in distinct excess, magnesic chloride mixture — in (92), (93), (94) and (95) 1.5 cm.³ and 1.5 cm.³ more after the precipitate had settled; in (96) and (97) 2 cm.³; in (98) and (99) 5 cm.³; in (100) and (101) 10 cm.³ drop by drop, and then 10 cm.³ more at once — and finally after the precipitate had settled, ammonia until the solution evolved a strong amoniacal odor.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
XIV.	(92)	0.0424 gr.	0.0271 gr.	0.0269 gr.	+ 0.0002 gr.	+ 0.74
	(93)	0.0427 gr.	0.0273 gr.	0.0269 gr.	+ 0.0004 gr.	+ 1.49
XV.	(94)	0.0428 gr.	0.0274 gr.	0.0269 gr.	+ 0.0005 gr.	+ 1.86
	(95)	0.0429 gr.	0.0274 gr.	0.0269 gr.	+ 0.0005 gr.	+ 1.86
XIV.	(96)	0.0430 gr.	0.0275 gr.	0.0269 gr.	+ 0.0006 gr.	+ 2.23
	(97)	0.0431 gr.	0.0276 gr.	0.0269 gr.	+ 0.0007 gr.	+ 2.60
	(98)	0.0436 gr.	0.0279 gr.	0.0269 gr.	+ 0.0010 gr.	+ 3.72
	(99)	0.0440 gr.	0.0281 gr.	0.0269 gr.	+ 0.0012 gr.	+ 4.46
XV.	(100)	0.0441 gr.	0.0282 gr.	0.0269 gr.	+ 0.0013 gr.	+ 4.83
	(101)	0.0447 gr.	0.0286 gr.	0.0269 gr.	+ 0.0017 gr.	+ 6.32

In experiments (102) to (115) inclusive 5 cm.^{3} of strong hydrochloric acid were added to each portion of phosphate and tungstate, and to portions (112), (113), (114) and (115) 0.5 gr. of citric acid; to every portion, excepting (108) and (109), ammonia in distinct excess; to (108) and (109) ammonia until the precipitate which formed at first was redissolved but not until the solution smelled of ammonia; to all, individually, 20 cm.^{3} of magnesic chloride mixture from which the ammonia had been expelled, and, after the settling of the precipitate, ammonia in strong excess.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
XV.	(102)	0.0436 gr.	0.0279 gr.	0.0269 gr.	+ 0.0010 gr.	+ 3.72
	(103)	0.0441 gr.	0.0282 gr.	0.0269 gr.	+ 0.0013 gr.	+ 4.83
XVI.	(104)	0.0446 gr.	0.0285 gr.	0.0269 gr.	+ 0.0016 gr.	+ 5.95
	(105)	0.0454 gr.	0.0290 gr.	0.0269 gr.	+ 0.0021 gr.	+ 7.80
	(106)	0.0459 gr.	0.0294 gr.	0.0269 gr.	+ 0.0025 gr	+ 9.29
	(107)	0.0465 gr.	0.0297 gr.	0.0269 gr.	+ 0.0025 gr.	+ 9.29
XV.	(108)	0.0498 gr.	0.0318 gr.	0.0269 gr.	+ 0.0049 gr.	+ 18.21
	(109)	0.0543 gr.	0.0347 gr.	0.0269 gr.	+ 0.0078 gr.	+ 28.99
IX.	(110)	0.3251 gr.	0.2079 gr.	0.2017 gr.	+ 0.0062 gr.	+ 3.04
	(111)	0.3262 gr.	0.2086 gr.	0.2017 gr.	+ 0.0069 gr.	+ 3.39
	(112)	0.3381 gr.	0.2178 gr.	0.2017 gr.	+ 0.0161 gr.	+ 7.91
	(113)	0.3398 gr.	0.2187 gr.	0.2017 gr.	+ 0.0170 gr.	+ 8.35
	(114)	0.3423 gr.	0.2190 gr.	0.2017 gr.	+ 0.0173 gr.	+ 8.49
	(115)	0.3429 gr.	0.2193 gr.	0.2017 gr.	+ 0.0176 gr.	+ 8.64

Phosphomolybdates.

In each of the following experiments upon the determination of phosphoric oxide in phosphomolybdates, 0.5 gr. of molybdic oxide (MO_3) were dissolved in ammonia and added

to 40 cm.³ of a phosphate solution, 5 cm.³ of strong hydrochloric acid added and ammonia in distinct excess. To portions (116) to (120) inclusive were added 20 cm.³ of magnesic chloride mixture, and to portions (121) to (122) 20 cm.³ of magnesic sulphate mixture. The first precipitates of (119), (120), (121) and (122) were filtered off on paper, dissolved in hydrochloric acid and thrown down again with ammonia, collected on asbestus (as the first precipitates of the other portions were), washed and ignited as usual. Portions (123) and (124) were precipitated with 1.5 cm.³ of magnesic chloride mixture, 1.5 cm.³ being added after the precipitate had settled, together with ammonia in strong excess. Portions (125) to (129) inclusive were precipitated with 20 cm.³ of magnesic chloride mixture from which the ammonia had been expelled, and ammonia was added in strong excess after the settling of the precipitate.

		$Mg_2P_2O_7$.	P_2O_5 found.	P_2O_5 required.	Error.	Per cent. error.
XII.	(116)	0.0441 gr.	0.0282 gr.	0.0270 gr.	+ 0.0012 gr.	+ 4.44
	(117)	0.0452 gr.	0.0289 gr.	0.0270 gr.	+ 0.0019 gr.	+ 7.04
	(118)	0.0458 gr.	0.0293 gr.	0.0270 gr.	+ 0.0023 gr.	+ 8.52
XIII.	(119)	0.0423 gr.	0.0271 gr.	0.0270 gr.	+ 0.0001 gr.	+ 0.37
	(120)	0.0425 gr.	0.0272 gr.	0.0270 gr.	+ 0.0002 gr.	+ 0.74
	(121)	0.0423 gr.	0.0271 gr.	0.0270 gr.	+ 0.0001 gr.	+ 0.37
	(122)	0.0427 gr.	0.0273 gr.	0.0270 gr.	+ 0.0003 gr.	+ 1.11
XVI.	(123)	0.0423 gr.	0.0270 gr.	0.0269 gr.	+ 0.0001 gr.	+ 0.37
	(124)	0.0424 gr.	0.0271 gr.	0.0269 gr.	+ 0.0002 gr.	+ 0.74
	(125)	0.0424 gr.	0.0271 gr.	0.0269 gr.	+ 0.0002 gr.	+ 0.74
	(126)	0.0425 gr.	0.0272 gr.	0.0269 gr.	+ 0.0003 gr.	+ 1.11
IX.	(127)	0.3168 gr.	0.2026 gr.	0.2017 gr.	+ 0.0009 gr.	+ 0.44
	(128)	0.3173 gr.	0.2030 gr.	0.2017 gr.	+ 0.0013 gr.	+ 0.64
	(129)	0.3180 gr.	0.2033 gr.	0.2015 gr.	+ 0.0016 gr.	+ 0.79

Experiments (1) to (10) inclusive (11), (13) and (15) demonstrate that the method of estimating the phosphoric oxide of alkaline phosphates by precipitation with magnesic sulphate mixture and washing until the chlorine reaction vanishes from the filtrate gives results far too high when the amount of the precipitant used is in any considerable excess of the amount theoretically required. Thus, in experiments (1) to (6), in each of which 20 cm.³ of magnesic sulphate mixture were used, the amount required by theory being about 5.2 cm.³, the

error varies from + 0.0033 gr. to + 0.0060 gr. on 0.1298 gr. of phosphoric oxide, or from + 2.54 to + 3.39 per cent.; in experiments (7) to (10), in each of which 20 cm.^{3} of the precipitant were used, while theory requires about 1.1 cm.^{3}, the error upon 0.0265 gr. of phosphoric oxide varies from + 0.0004 gr. to + 0.0021 gr., or from + 1.51 to + 7.92 per cent.; in experiment (11) in which 6 cm.^{3} of the precipitant were used, while about 2.1 cm.^{3} were theoretically required, the error is + 0.0007 gr. upon 0.0512 gr. of phosphoric oxide, or + 1.37 per cent.; and in experiments (13) and (15), in which 12 cm.^{3} of the precipitant were used, while about 2.1 cm.^{3} were theoretically required, the error upon 0.0512 gr. of phosphoric oxide was + 0.0017 gr., or + 3.31 per cent.

Experiments (21) to (26) inclusive show that when the process was varied so as to precipitate the phosphate solution, either containing no free ammonia or a very small quantity, by a magnesic sulphate mixture from which the ammonia had been expelled, the error of the result varied from + 0.0061 gr. to + 0.0117 gr. upon 0.1875 gr. of phosphoric oxide, or from + 3.25 to + 6.24 per cent.; and from + 0.0077 gr. to + 0.0106 gr. upon 0,2142 gr. of phosphoric oxide, or from + 3.59 to + 4.94 per cent.— the greatest errors appearing naturally in the experiments made with hot solutions containing no free ammonia in which cases the hydro-magnesic phosphate first thrown down was partially changed into tri-magnesic phosphate by the action of the heat, and therefore not converted into ammonio-magnesic phosphate upon the subsequent addition of ammonia.

Experiments (12), (14), (16) and (17) to (20) inclusive indicate that tolerably good results may be obtained by draining the first precipitate, dissolving in hydrochloric acid and reprecipitating with ammonia; the first three experiments showing incidentally that the addition of small amounts of citric acid does not prevent precipitation to any very marked degree in presence of a considerable excess — in this case about 10 cm.^{3} to 0.5 gr. of citric acid — of magnesic sulphate mixture. Thus in experiments (12), (14) and (16) the error was 0; and in experiments (17) to (20) the error varied from + 0.0006 gr. to + 0.0015 gr. on 0.1863 gr. of phosphoric oxide, or from + 0.32 to + 0.80 per cent., the mean error being about + 0.0006 gr., or + 0.32 per cent.

It appears from these experiments that the method of precipitating by magnesic sulphate mixture without the solution and second precipitation ought to give an accurate determination of phosphoric acid, providing only that the amount of the precipitant used were just sufficient to complete the precipitation. But this condition renders the process practically useless in ordinary cases; and inasmuch as in Kissel's method of compensating for enclosed material by excessive washing, the amount of washing must necessarily be proportioned both to the weight of phosphoric acid present and to the excess of the precipitant,— elements which introduce a great deal of uncertainty,— it would appear that if magnesic sulphate mixture is to be the precipitant the method of precipitating twice is the only one which can be relied upon on all occasions to give tolerably correct results.

The results obtained in experiments (27) to (66) by precipitating with magnesic chloride mixture are different as the method of treatment varies. It will be noticed that in experiments otherwise essentially similar the variations in the amount of the precipitant produce differences in the results. Thus, in experiments (27) to (43), in which 10 cm.^{3} or 12 cm.^{3} of the precipitant were used, the error varies from — 0.0008 gr. to + 0.0012 gr., or from — 0.42 to + 0.64 per cent., the mean error being nearly 0; while in the experiments (48) to to (53), in which 40 cm.^{3} of the precipitant were used, the error varies from + 0.0011 gr. to + 0.0016 gr., or from + 0.60 to + 0.87 per cent., the mean error being about + 0.0013 gr., or + 0.71 per cent. It will be seen also that while it makes no apparent difference whether the precipitant is added to the phosphate directly, as in (27) and (28), or after treatment with hydrochloric acid, as in (29) to (39), the dissolving of a precipitate, by adding hydrochloric acid to the supernatant liquid, and reprecipitation with ammonia tend to reduce the results below those of experiments in which this has not been done, but which are similar in other respects. This appears very distinctly in a comparison of experiments (40) and (41) with (42) and (43), where the mean error is reduced from about + 0.0010 gr. upon 0.1875 gr. of phosphoric oxide, or from + 0.56 per cent. to 0; or of experiments (44) and (45) with (46) and (47), where the mean error is reduced from

+ 0.0022 gr. to about + 0.0003 gr. upon 0.1885 gr. of phosphoric oxide, or from + 1.17 to + 0.18 per cent.

It appears, further, from a comparison of experiments (54) to (58) with experiments (48) to (53), that results got by precipitating solutions containing either no free ammonia, as in (56), (57) and (58), or only a small amount, as in (54) and (55), by a magnesic chloride mixture deprived of ammonia are more nearly correct than those got by precipitating under essentially similar conditions with the ammoniacal magnesic chloride mixture, as in (48) to (53). Thus, in (48) to (53) the error varies from + 0.0011 gr. to + 0.0016 gr. upon 0.1831 gr. of phosphoric oxide, or from + 0.60 to + 0.87 per cent., the mean error being about + 0.0013 gr. or + 0.71 per cent.; while in (54) to (58) the error varies from 0 to + 0.0012 gr. upon 0.1831 gr. or 0.1875 gr. of phosphoric oxide, or from 0 to 0.64 per cent., the mean error being about + 0.0004 gr. or + 0.22 per cent.; and it is to be remarked that in (54), (55) and (56), in which dilute ammonia was added after the non-ammoniacal magnesic chloride mixture, the mean error — about + 0.0002 gr. or + 0.10 per cent.—is much smaller than the mean error of (57) and (58)—about + 0.0008 gr., or + 0.44 per cent.—in which strong ammonia was added after the non-ammoniacal magnesic chloride mixture. The high results of experiments (59) and (60), in which the non-ammoniacal magnesic chloride mixture was added to the hot phosphate solution, are explained by the fact that a part of the hydro-magnesic phosphate first formed was decomposed by the heat with the formation of trimagnesic phosphate, and therefore not completely converted into ammonio-magnesic phosphate by the ammonia subsequently added. From experiments (61) to (64) it will be seen that the presence of 3 gr. of sodic chloride in the phosphate solution raises the figures of the analysis materially when precipitation is effected by the ammoniacal magnesic chloride mixture, even with small weights of phosphoric oxide, and that better results are got in (65) and (66) by using the non-ammoniacal mixture.

The use of an excessive quantity, too, of ammonic chloride tends apparently to reduce the error. Thus, in experiments (48) to (53) the mean error was about + 0.0013 gr., or + 0.71 per cent., while in (44) and (45), in which free ammonia, but

no ammonic chloride beyond the amount in the magnesic chloride mixture, was used, the mean error is + 0.0022 or + 1.17 per cent., although less of the precipitant was used in the latter.

The cause of all these differences in the accuracy of the determination of the phosphoric oxide of alkaline phosphates by precipitation with magnesic chloride mixture seems to lie in the variations of the rapidity with which the ammonio-magnesic phosphate is crystallized from solution. The sudden addition of a large amount of the precipitant, or of an excess of the precipitant to a strongly ammoniacal solution of the phosphate, or of strong ammonia to a solution of the precipitate in acid, tends to hasten the deposition, and so to prevent the complete exclusion of foreign material from the crystalline structure; while in the precipitation of solutions containing large amounts of ammonic chloride, or of weakly ammoniacal solutions, or of solutions of the precipitate in acid, by the gradual addition of ammonia the process of crystallization goes on more slowly and perfectly.

The differences between results got by using a magnesic sulphate mixture and those obtained with a magnesic chloride mixture may be, perhaps, partly explained by the supposition that magnesic sulphate resists exclusion during the crystallization of the ammonia-magnesic phosphate more effectively than magnesic chloride, and partly by the fact that magnesic sulphate enclosed in a precipitate would probably not change materially in composition during an ignition over a Bunsen burner in a crucible standing on platinum foil, while magnesic chloride ignited in presence of aqueous vapor under like circumstances would be converted into magnesic oxide whose molecular weight is but one-third of that of the sulphate. It is difficult, at all events, to conceive how the contamination of the precipitate can be other than mechanical; for the trimagnesic phosphate could only be produced by a reaction between the ammonio-magnesic phosphate and magnesic sulphate,— which is quite improbable, at least in the cold,— and the formation of a magnesic hydrate or basic sulphate would seem to be altogether unlikely under the circumstances.

In the experiments upon the phosphotungstates the mean error of the method involving a single precipitation with magnesic sulphate mixture (experiments 67 to 70) was about + 0.0021 gr. upon 0.0265 gr. and with magnesic chloride mixture (experiments 80 to 84) about + 0.0024 gr., upon 0.0266 gr. or 0.0269 gr., of phosphoric oxide, or about + 8.44 per cent. The mean error of the method of double precipitation upon nearly the same amounts of phosphoric oxide, the precipitant alone being used to wash the first precipitate and no citrate being present, was, with magnesic sulphate mixture (experiments 75 to 79) about + 0.0004 gr., or + 1.51 per cent., and with magnesic chloride mixture (experiments 89 to 91) + 0.0002 gr., or + 0.74 per cent.; the mean error when the first precipitate by magnesic sulphate mixture was washed with the precipitant and afterwards with ammonia water (experiments 71 to 74) being about —0.0015 gr., or —5.66 per cent.; and when the first precipitate was thrown down in presence of a citrate by magnesic chloride mixture and washed with the precipitant (experiments 85 to 88), about — 0.0007 gr., or — 2.59 per cent. When precipitation was effected with 1.5 cm.^{3} of magnesic chloride mixture, the same being added after precipitation (experiments 92 to 95) the mean error upon 0.0269 gr. of phosphoric oxide was + 0.0004 gr. or + 1.49 per cent.; when by 2 cm.^{3} (experiments 96 and 97) about + 0.0006 gr., or + 2.23 per cent.; when by 5 cm.^{3} (experiments 98 and 99) + 0.0011 gr., or + 4.09 per cent.: and when by 10 cm.^{3} added drop by drop, with 10 cm.^{3} more subsequent to precipitation (experiments 100 and 101) + 0.0015 gr., or + 5.58 per cent. The mean error of the determination by precipitating with 20 cm.^{3} of non-ammoniacal magnesic chloride mixture, in slightly ammoniacal solutions (experiments 102 to 107 and 110 to 115) was about + 0.0018 gr. upon 0.0269 gr. of phosphoric oxide, or + 6.69 per cent.; about + 0.0065 gr. upon 0.2017 gr. of phosphoric oxide, or + 3.22 per cent., in solutions containing no citrate, and in solutions containing a citrate + 0.0170 gr., or + 8.35 per cent. The mean error when 20 cm.^{3} of non-ammoniacal magnesic chloride mixture was added to the solution of phosphate and tungstate containing no free ammonia (experiments 108 and 109) amounted to about + 0.0063 gr. upon 0.0269 gr. of phosphoric oxide, or + 23.60 per cent.

The use of citric acid in many of the experiments above, in accordance with a suggestion of Dr. Gibbs, appears to be attended with unfavorable results. Thus in experiments (85) to (88), in which the first precipitates were dissolved and re-precipitated, this appears to have lowered the results below those of (89) to (91); while in experiments (80) to (82) and in experiments (112) to (115), in which the first precipitate was not dissolved, it appears to have raised the results above those of (83) and (84), and (110) and (111) respectively,— facts which are perhaps to be explained by attributing to the citrate both a solvent and contaminating action upon the precipitate.

Of the experiments upon the phosphomolybdates (123) and (124), in which the precipitation was effected by 1.5 cm.^{3} of magnesic chloride mixture, 1.5 cm.^{3} of the same being added afterward, show a mean error of less than + 0.0002 gr. upon 0.0269 gr. of phosphoric oxide, or + 0.55 per cent.; and experiments (116) to (118) in which 20 cm.^{3} of the same precipitant were employed + 0.0018 gr. upon 0.0270 gr. of phosphoric oxide, or + 6.66 per cent.; experiments (119) to (122), in two of which the precipitation was effected by magnesic sulphate mixture, and in two by magnesic chloride mixture, the first precipitate being washed with the precipitant, dissolved in hydrochloric acid and again thrown down, less than + 0.0002 gr. upon 0.0270 gr. of phosphoric oxide, or + 0.65 per cent. In experiments (125) to (129) in which 20 cm.^{3} of the magnesic chloride mixture deprived of ammonia were added to slightly ammoniacal solutions, the mean error was less than + 0.0003 gr. on 0.0269 gr. of phosphoric oxide, or + 0.92 per cent., and less than + 0.0013 gr. on 0.2017 gr. of phosphoric oxide, or + 0.62 per cent.

It will be noticed that in the experiments with phosphates and phosphomolybdates a large excess of the magnesic chloride mixture was not markedly prejudicial to the accuracy of results when precautions were taken to induce a slow formation of the precipitate, while in the experiments with phosphotungstates the reverse was true. The reason for this exceptionally unfavorable action in the case of the phosphotungstates is probably indicated in the facts that the addition of free ammonia beyond a certain amount to the solution of a

phosphotungstate produces turbidity, and that the addition of magnesia mixture to a clear solution of normal sodic tungstate, ammonic chloride and ammonia renders the solution opalescent and occasions the deposition, after some hours, of an almost invisible precipitate; but it is to be noted in this connection that the action of magnesia mixture upon a clear ammoniacal solution of ammonic molybdate and ammonic chloride is similar to its action upon the tungstate solution.

Summary.

It would appear from the preceding account that in determining the phosphoric oxide of alkaline phosphates, free from sulphates or other substances likely to contaminate a precipitate, accuracy is most conveniently and surely attained by adding to the somewhat dilute solution of the phosphate ammonia in slight but quite distinct excess, then an excess of magnesic chloride mixture containing no free ammonia (made by dissolving three parts of crystallized magnesic chloride and eight parts of ammonic chloride in water, adding water containing ammonia until the volume of the solution reaches forty-eight parts, filtering and boiling off the free ammonia), and, after the precipitate has settled, ammonia until the liquid evolves a strong odor of it. In determining the phosphoric oxide of phosphotungstates the best results are to be got by adding to the solution containing free ammonia an excess of either of the magnesia mixtures, washing the precipitate with the precipitant, dissolving in hydrochloric acid, diluting if necessary and reprecipitating with a little dilute ammonia, adding strong ammonia after the precipitate has settled; or, when working with small amounts, by proceeding as in the case of the phosphates, taking special care, however, that the solution is distinctly ammoniacal before precipitating, and that no great excess of the precipitant is used. In the determination of the phosphoric oxide of phosphomolybdates, the method recommended for use in the case of the phosphates serves very well when the amount of phosphoric oxide does not exceed (let us say) 0.05 gr., but for amounts larger than this the method of double precipitation recommended for the phosphotungstates is more accurate.

As to the time which should be allowed to pass between

precipitating and filtering, my experiments support those of Abesser, Jani, and Maercker * in pointing to the condition that a precipitate may be filtered with safety as soon as it has completely subsided, or, after ten or fifteen minutes.

The use, for the filtration and ignition of the precipitate, of the method which I have employed in the experiments described above greatly expedites the analysis. Thus, with two perforated crucibles at my disposal, I have completed within four and one-half hours from the measuring out of the first solution seven determinations of the phosphoric oxide of an alkaline phosphate,— the ignition of each precipitate requiring less than five minutes.

LABORATORY NOTES.

By Arthur Michael.

I.—ON MONO-ETHYLPHTHALATE.

The aim of the following experiments, made several years ago, was the preparation of ortho-formylbenzoic acid, and for which purpose mono-ethylphthalate was subjected to the action of phosphorus trichloride, in the hope of obtaining the chloride of that compound, which I intended to reduce with nascent hydrogen.

To prepare mono-ethylphthalate absolute alcohol was allowed to act on phthalic anhydride, a reaction similar to that of the formation of mono-ethylsuccinate by the action of alcohol on succinic anhydride.† Equal parts of absolute alcohol and phthalic anhydride were heated in a flask connected with an upright condenser for ten hours at 100°. The whole of the anhydride was never converted into the ether in question, even if the time of heating was prolonged and the relative amount of alcohol to anhydride greatly increased. The excess of alcohol was evaporated at a low

*Zeitschrift f. anal. Chem. XII. 250. †Heintz, Pogg. Ann. 108, 70.

temperature, and the residue which remained was dissolved in water and neutralized in the cold with pure barium carbonate, thus forming the barium salts of mono-ethylphthalate and phthalic acid. To effect a separation of the two salts advantage was taken of their different solubility in water; the former salt being extremely soluble in moderately warm water, whereas barium phthalate is much less soluble. The precipitate which settled on neutralization was therefore barium phthalate, and by evaporating the filtrate from this precipitate to a small bulk, and filtering the solution while warm from the precipitate which had then settled, and, if necessary, repeating the operation again, the two barium salts were easily separated. The filtrate yielded on cooling the barium salt of the new acid in long, concentrically grouped, white needles, which are very soluble in cold and in all proportions in warm water.

The barium analyses showed that this salt has the formula $\left(C_6H_4\begin{matrix}COOC_2H_5\\COO\end{matrix}\right)_2Ba$.

.5360 gr. of substance, dried at 100°, gave .2405 gr. of barium sulphate.

.6812 gr. gave .3148 gr. of barium sulphate.

			Found.	
		Calculated.	I.	II.
Ba.	...	27.24	26.83	27.17

A concentrated aqueous solution of the barium salt is precipitated by silver nitrate, forming the corresponding silver salt. This salt crystallizes from water in beautiful, long needles, which on exposure to the light soon blacken. They are moderately soluble in cold and quite soluble in warm water.

The results of the silver analyses correspond with the formula $C_6H_4\begin{matrix}COOC_2H_5\\COOAg.\end{matrix}$

.5210 gr. of substance, dried in vacuo, gave, after ignition, .1883 gr. of metallic silver.

.6364 gr. gave .2314 gr. of silver.

.5776 gr. gave .2078 gr. of silver.

			Found.		
		Calculated.	I.	II.	III.
Ag	...	35.88	36.11	36.33	35.98

The free mono-ethylphthlate was easily obtained by treating an aqueous solution of the barium salt with the calculated amount of sulphuric acid, and evaporating the filtrate from the barium sulphate in vacuo, and is a heavy oil which is moderately soluble in water. It is remarkably unstable towards heat; upon distillation it decomposes in phthalic anhydride and alcohol, and gradually undergoes the same decomposition when heated upon a water-bath.

To obtain the chloride, $C_6H_4\begin{cases}COOC_2H_5\\COCl\end{cases}$, equivalent quantities of mono-ethylphthalate and phosphorus trichloride were mixed in a retort connected with a condenser, and, finding that no reaction ensued in the cold, the retort was gently warmed on a water-bath. The reaction was quite violent, and a considerable quantity of chlorhydric acid was evolved. The contents of the retort were then treated with cold water, and left a heavy oil, which was dried over H_2SO_4 in vacuo.

The oil was found to be free from chlorine. A proximate analysis gave results which correspond with the formula of di-ethylphthalate, and a comparison of the properties and boiling points of the two substances showed them to be identical.

.2218 gr. of substance gave .5284 gr. of CO_2 and .1301 gr. of H_2O.

	Calculated for $C_6H_4(COOC_2H_5)_2$	Found.
C ...	64.86	64.97
H ...	6.30	6.52

The reaction, evidently, proceeded quite differently from that anticipated, and I deemed it advisable to examine the gases formed in the reaction more thoroughly. On passing the gases evolved through water only a portion was absorbed, which proved to be chlorhydric acid; the unabsorbed portion burned with a green flame and contained chlorine. On passing through a tube placed in a cooling mixture it condensed to a volatile liquid, which proved to be ethylchloride.

The first step in the above described reaction is doubtless the formation of $C_6H_4\begin{cases}COOC_2H_5\\COCl\end{cases}$, a reaction which may be expressed by the equation:

$$3C_6H_4\begin{cases}COOC_2H_5\\COOH\end{cases} + PCl_3 = 3C_6H_4\begin{cases}COOC_2H_5\\COCl\end{cases} + P(OH)_3.$$

But the chloride of mono-ethylphthalate possesses that remarkable property of the phthalic compounds of undergoing easily a condensation, and even at the temperature of the reaction it decomposes into phthalic anhydride and ethylchloride:

$$C_6H_4\begin{cases}COOC_2H_5\\COCl\end{cases} = C_6H_4\begin{cases}CO\\CO\end{cases}O + C_2H_5Cl.$$

To explain the formation of di-ethylphthalate, we may suppose that part of the ethylchloride acted on unchanged mono-ethylphthalate, forming chlorhydric acid and di-ethylphthalate.

The action of phosphorus pentachloride on mono-ethylphthalate proceeded in the cold, and I hoped to obtain the chloride in this way; but I found the reaction was in this case similar to that of the trichloride, the same products being formed.

The described reaction illustrates well the condensation power of the phthalic compounds, since the analogous compounds $\begin{matrix}COOC_2H_5\\COCl\end{matrix}$ and $C_6H_4\begin{cases}COOC_2H_5\\COOH\end{cases}$ can both be distilled without undergoing decomposition.

II.—ON A NEW FORMATION OF ETHYL-MUSTARD OIL.

A. W. Hofmann,* shortly after Gautier and himself demonstrated that the alkylcarbamines could be obtained by the action of alkyliodides on silver cyanide, examined the action of ethyliodide on silver sulphocyanate, in the hope of obtaining ethyl-mustard oil. He found, however, that only ethyl-sulphocyanate was formed in the reaction. Several years later, V. Meyer,† after the remarkable results obtained from silver nitrite, repeated this experiment, and obtained as result the sulphocyanate free from even the slightest trace of mustard oil. These results evidently indicate, that the silver atom in silver sulphocyanate is joined with the sulphur and not with the nitrogen atom, a molecular juxtaposition which is doubtless owing to the greater affinity of silver for sulphur than for nitrogen.

It seemed possible by employing a metallic sulphocyanate, in which the metal had a greater affinity for nitrogen and a

* Monatsber. d. ber. Acad. 1867, 650. † Ann. Chem. 171, 47.

less affinity for sulphur than silver, that mustard oils might be obtained by the action of alkyliodides on such a salt. I was therefore induced to reinvestigate the action of ethyl iodide on mercuric sulphocyanate. Schlagdenhauffen* had already made this experiment; he obtained ethylsulphocyanate and a red mass, which was not further examined.

Ethyliodide acts on mercuric sulphocyanate even at 100°, but I found it advisable to heat the mixture at a higher temperature. For this purpose a tube containing 20 gr. of $Hg(SCN)_2$ and 30 gr. of C_2H_5I was heated for about two and one-half hours at 140–150°. Upon opening the tube the strong penetrating odor of ethyl-mustard oil was observed, and a dark red sediment had formed. The contents of the tube were brought into a flask connected with a condenser, and treated with steam as long as an oil passed over. This oil was separated from the supernatant water, dried over calcium chloride and distilled; that portion which passed over under 135° was collected separately. The penetrating odor of this portion indicated the presence of ethyl-mustard oil in it, but the small quantity of oil obtained, although I had used a number of the tubes, only allowed a very imperfect separation from the sulphocyanate, which is formed in much greater quantity in the reaction than its isomer. To prove the presence of ethyl-mustard oil in the lower boiling portion it was mixed with aniline, and the mixture allowed to stand for several days. A crystalline precipitate gradually settled from the liquid, which also lost the odor of mustard oil and had now that of ethyl-sulphocyanate. The precipitate was purified by crystallization from water, and a comparison of its properties with those of phenyl-ethyl-sulphocarbamide† showed that the two compounds were identical, thus proving indirectly the presence of ethyl-mustard oil in the original liquid. The amount of mustard oil formed in this reaction is very small — I should judge about three per cent. of the amount of sulphocyanate; but even this compound is formed in quantities which are very small in comparison to the amount of the ingredients employed. The red mass mentioned by Schlagenhauffen is the principal product of the reaction. This red compound is possibly a

*Ann. ch. phys. (3), 56, 297. † Weith—Deutsch. ch. Gesell. Ber 1875, 1524.

double compound of ethyl-mustard oil with mercuric iodide; it contains Hg, C, S and I. It yields upon distillation a heavy oil containing sulphur. I hoped to decompose it by boiling with a concentrated aqueous solution of potassium cyanide, as Gautier decomposed the compound $C_2H_5NCAgNC$, but it proved to be without action on it.

Methyl and amyl iodides acted in a similar manner on mercuric sulphocyanate, and formed liquids which had the strong penetrating odor of mustard oils. Although the method is of no importance for the preparation of mustard oils, still it is of theoretical interest as characterizing an important difference in the action of paraffin iodides on the mercuric and silver salts of sulphocyanic acid.

III.—ON THE PREPARATION OF METHYL ALDEHYDE.

I have lately had occasion to use a considerable quantity of methyl aldehyde, and found that the methods hitherto in use only permitted its preparation in large amounts with much difficulty. This is the case with the method of Butlerow* and that of Heintz.† The method recently proposed by A. W. Hofmann,‡ by the oxidation of methyl alcohol, yields a dilute methylalcoholic solution of the aldehyde, but this solution is much less adapted to my purpose than an aqueous solution. I have found that the action of water on mono-chlormethylacetate, a compound discovered by L. Henry § by the action of chlorine on methylacetate, yields almost the theoretical amount of an aqueous solution of methyl aldehyde.

For the preparation of mono-chlormethylacetate 500 gr. of methylacetate were placed in a flask surrounded by cold water and connected with a condenser, and a current of dry chlorine gas passed through the liquid in the flask for about seven hours. The contents of the flask were distilled, and that portion distilling between 90–130° was finally redistilled; the portion which now passed over between 100–120° was mono-

* Ann. Chem. Pharm. 144, 38.

† Ann. Chem. Pharm. 138, 40.

‡ Ber. d. chem. Gesell. 1878, 1685.—The formation of methylaldehyde by the oxidation of methylalcohol may easily be shown in the lecture-room by allowing a drop of methylalcohol to fall on a heated platinum crucible so that it takes a spheroidal state; the strong penetrating odor of the aldehyde is almost immediately noticed.

§ Ber. d. chem. Gesell. 1873, 42.

chlormethylacetate. The portion boiling under 100° may be again subjected to the action of chlorine, and yields a further quantity of mono-chlormethylacetate. The yield of the mono-chlor-compound is very satisfactory, and it may be obtained in this manner in large quantities.

Henry, in the above-mentioned memoir, has already called attention to the fact that this compound is easily decomposed by alkalis, and gives rise to the odor of methyl aldehyde. It is, however, preferable to decompose it with water. For this purpose 110 gr. of mono-chlormethylacetate and 55 gr. of distilled water were heated in a strong, closed flask for about one-half to one hour* at 100°. The water, which at first formed a layer over the ether, mixed, after being heated for that time, to form a homogeneous liquid, which smelt strongly of methyl aldehyde. The contents of the flask were neutralized exactly with a very concentrated solution of sodium hydrate, about 73 gr. of that compound being necessary to neutralize the amount taken. The solution thus obtained was distilled from a flask placed in an oil-bath, and yielded a colorless distillate, which was usually slightly acid, and which was easily obtained neutral by a subsequent neutralization and distillation. The white solid remaining in the flask consisted of sodium chloride and acetate. From 110 gr. of chlormethylacetate about 140–150 gr. of the aqueous solution were obtained, and which contained 16 to 18 per cent. of methyl aldehyde, as the following estimations show:

13 gr. of solution treated with H_2S yielded 2.34 gr. of thioformaldehyde.

20 gr. yielded 3.28 gr. of thioaldehyde.

The formation of methylaldehyde by the action of water on mono-chlormethylacetate may be expressed by the equation:

$$CH_2\begin{matrix}Cl\\ \diagup\\ \diagdown\\ O\end{matrix} - OC - CH_3 + H_2O = CH_2O + C_2H_4O_2 + HCl.$$

10 gr. of mono-chlorether should yield, according to this equation, 2.76 gr. of CH_2O, and 2.34 gr. were obtained, that is, 81 per cent. of the theoretical yield.

Trioxymethylene may be obtained from the solution in question by allowing it to evaporate in vacuo, but not without considerable loss; 26 gr. of solution yielded 2.17 gr. of

* If heated too long the flask opened under strong pressure.

trioxymethylene, which is about 40 per cent. of the theoretical yield. The aqueous solution of methyl aldehyde evaporates in vacuo to about one-third of its original bulk before a separation of trioxymethylene begins, and in this manner an aqueous solution containing about 40 per cent. of methyl aldehyde may be obtained.

This method has allowed me to obtain a large quantity of methyl aldehyde, and to examine its behavior towards potassium and sodium salts, as well as the alkaline bases. I have obtained very interesting results, which I shall describe later.

IV.—ON THE "MIGRATION OF ATOMS IN THE MOLECULE" AND REIMER'S CHLOROFORM ALDEHYDE REACTION.

The formation of a liquid in the action of aniline chlorhydrate on methyl alcohol at a high temperature, which boiled at a higher temperature than dimethylaniline, was first observed by Chas. Lauth,* and he considered the liquid thus formed as consisting of polymers of that compound. Several years later A. W. Hofmann and C. A. Martius† examined this oil more thoroughly, and succeeded in isolating from it dimethyltoluidine, and even higher homologues of dimethylaniline. Hofmann and Martius explained the formation of these compounds in that the methyl chloride formed in the reaction, after having substituted the hydrogen atoms of the amido-group, attacked the hydrogen of the benzene nucleus. Later, Hofmann,‡ in a remarkable memoir, again returned to this subject, and by a series of interesting experiments threw new light on the nature of this reaction. He stated that naturally the formation of tri-methylphenylammonium chloride would, in the first place, be expected, and was therefore induced to examine the behavior of the corresponding iodide under similar conditions towards heat. This compound yielded, when heated at 230°C. in a closed tube, a mixture of two isomeric toluidines and methylxylidine; at the temperature of melting lead, cumidine. The explanation given by Hofmann of these facts is the "migration of atoms in the molecule," the methylgroups changing places with the hydrogen atoms of the benzene nucleus.

* Bull. soc. chim. [2] 7, 448. † Ber. d. chem. Gesell. 1871, 742.
‡ Ber. d. chem. Gesell. 1872, 704.

It seemed to me that by considering the behavior of the tetra-alkylammonium halogens on distillation a more intimate knowledge of the nature of the reaction in question might be obtained. These compounds decompose at a high temperature into tri-alkylamines and alkylhalogens. Bearing on this subject is also the behavior of the haloid acid salts of di- and tri-alkylamines towards heat, and which decompose into mono- and di-alkylamines and alkylhalogens.

Let us now consider the behavior of tri-methylphenylammonium iodide when heated in a closed tube at a high temperature. The first result would be its decomposition into di-methylaniline and methyl iodide; and when we consider the facility with which benzoylchloride, chloroform, phosphorus tri-chloride and other halogen compounds act on the hydrogen of the benzene nucleus in di-methylaniline, there is little doubt that under the favorable conditions of a high temperature, and where the direct combination is impossible, the methyl iodide would act on the hydrogen of the benzene nucleus, forming di-methyltoluidine and iodhydric acid. The acid thus formed then acts on the di-methyltoluidine,* forming mono-methyltoluidine and methyl iodide. The latter compound acts on the hydrogen of the nucleus forming monomethylxylidine and methyl iodide; and these compounds again reacting in a like manner, give as final products iodhydric acid and cumidine. That a higher temperature is necessary to realize the two last steps of the reaction, is owing to the stability of the dimethyltoluidine towards iodhydric acid at a temperature at which tri-methylphenylammonium iodide already decomposes into dimethylaniline and methyl iodide.

By the action of aniline chlorhydrate on an excess of methyl alcohol Hofmann and Martius obtained, as already mentioned, homologues of dimethylaniline. This result is due to the facility with which chlorhydric acid acts on methyl alcohol, and it is easy to understand that, in this case, aniline chlorhydate would be finally converted in penta-methyldimethylaniline chlorhydrate, providing sufficient methyl alcohol were present, and the time of heating sufficiently prolonged. Hofmann † also examined the behavior of the chlor-

* Methyltoluidine distilled in a current of chlorhydric acid yields toluidine and methylchloride.—Lauth (Bull. soc. chim. [2] 19, 489).

† Deutsch. ch. Ges. Ber. 1872, 790.

and iodhydrates of mono-methylaniline in a closed tube at 350°, and found that the former salt yielded para-toluidine, while from the latter salt the ortho-compound was obtained. That methyl chloride and iodide should form isomers in their action on the hydrogen of the benzene nucleus would not be in the least unexpected; but I believe a clue to the different results obtained in these *reactions* will be found in the greater stability of methylaniline chlorhydrate towards heat, than the jodhydrate of the base. It is hardly necessary to mention instances in which when both ortho- and para-substitution products of benzene are simultaneously formed, where the relative amount of each of the isomers formed depends on the temperature at which the reaction proceeded; the ortho-derivative predominating when a moderate, and the para-compound when a high temperature is employed. If then the iodhydrate decomposes into aniline and methyl iodide at a temperature lower than the chlorhydrate does into aniline and methyl chloride, it would naturally tend to form an ortho-derivative. Moreover, it is very probable that methyl iodide is able to substitute the hydrogen of the nucleus at a lower temperature than methyl chloride, and this property doubtless plays a role in the different results obtained.

The above considerations make it probable that were the vapors of methyl chloride and aniline, both heated to a temperature above that at which methylaniline chlorhydrate decomposes into methyl chloride and aniline, and the gases mixed at this temperature, para-toluidine would in this manner be formed.

A reaction apparently of an altogether different nature from that we have just considered, is the formation of ortho- and para-oxybenzoic aldehydes by the action of an aqueous solution of sodium hydrate and chloroform on phenol, which was discovered by K. Reimer* in 1876. Reimer and Tiemann,† in a subsequent paper, called attention to the analogy of the reaction in question to that of the formation of salicylic acid, by the action of carbonic acid on sodium *phenolate*, since the formic acid containing an atom less of oxygen than carbonic acid, would, therefore, form the aldehyde corresponding to the acid obtained by the action of carbonic acid. H. Kolbe‡

* Ber. d. chem. Gesell. 1876, 423. † Ibid. 1876, 826. ‡ J. p. Chem. (N. F), 14, 332.

lays stress on the fact that the formic acid which enters into this reaction is in a nascent state; the reaction expressed graphically is:

$$C_6H_5ONa + HCOOH = C_6H_4\begin{cases}ONa\\CHO\end{cases} + H_2O.$$

But can we well suppose that formic acid formed in the presence of a strong alkali would not immediately enter into chemical combination with it, to form a formate? It was, however, a question of experiment whether formic acid would act on a mixture of sodium hydrate and phenol to form aromatic oxy-aldehydes, and all experiments in this direction have given negative results. Evidently, if formic acid is the means of introducing the formyl group in phenol, it must have properties which are quite different from those of the acid commonly understood under this name, and, in fact, both Kolbe, and Reimer and Tiemann, attach importance to the fact that the acid entering into this reaction is in a nascent state. But, we may ask, how explain the different properties of nascent and free formic acid? Is it not the same acid, and in the same molecular state?

The comparison between the action of carbonic acid and chloroform and sodium hydrate, would be doubtless correct were carbon monoxide the principal product formed in the latter reaction. That it may be formed appears not improbable, since we know that Geuther* noticed its formation by the action of a dilute alcoholic solution of potassium hydrate on chloroform. But this view is also open to serious objections: firstly, the formation of carbon monoxide in the reaction of Reimer could hardly have escaped notice; secondly, the amount of carbon monoxide, if formed, would not justify the yield obtained of aldehydes; and finally, numerous attempts to obtain salicylic aldehyde by the action of free as well as nascent carbon monoxide have not succeeded.

There is still an hypothesis which appears to me to explain the reaction in question more satisfactorily, than those we have just considered. The action of an aqueous solution of sodium hydrate on chloroform proceeds very slowly, even on boiling. We have, however, in sodium hydrate a compound which possesses a strong affinity for chlorhydric acid, and we

* Ann. Chem. Pharm. 123, 121.

can easily understand that the alkali should extract the component parts of chlorhydric acid from sodium phenolate and chloroform; the hydrogen can, of course, only come from the benzene nucleus of the phenolate:

$$C_6H_5ONa + CCl_3H + NaHO = C_6H_4\begin{cases}ONa\\CCl_2H\end{cases} + NaCl + H_2O.$$

The compound first formed is, therefore, sodium oxybenzylidenchloride, the salt of a compound discovered by L. Henry,* and this salt is doubtless soluble in the solution in which it is formed. We know, however, that benzylidenchloride in an alcoholic alkaline solution is easily converted into benzoic aldehyde,† and there is no reason to doubt that sodium oxybenzylidenchloride under the influence of the excess of sodium hydrate employed in the reaction would undergo a like decomposition, thus forming the sodium salt of an oxy-aldehyde and sodium chloride:

$$C_6H_4\begin{cases}ONa\\CHCl_2\end{cases} + 2NaHO = C_6H_4\begin{cases}ONa\\CHO\end{cases} + 2KCl + H_2O.$$

It is easy to mention well-characterized reactions which bear a strong analogy to the reaction of Reimer, when it is considered in this light. For instance, the formation of the compound $C_6H_5—PCl_2$ by the action of phosphorus trichloride on benzene‡ resembles the first step, and that this compound yields on contact with water $C_6H_5P(OH)_2$, corresponds with the second step of the Reimer reaction. Again, the formation of triphenylmethane by the action of aluminium chloride on a mixture of chloroform and benzene is similar. The first step of this is doubtless the formation of benzylidenchloride; and were this compound formed in the presence of an alcoholic alkaline solution, or even, perhaps, a metallic oxide, benzoic aldehyde would probably be formed. It is hardly necessary to call attention to the fact that the hydrogen atoms in the nucleus of phenol show a much greater reactive power than those of benzene, and that the conditions under which the formyl group is introduced, by the action of sodium hydrate and chloroform on phenol, are especially favorable for this reaction.

The results obtained by Reimer and Tiemann§ by the action of sodium hydrate and chloroform on para-oxybenzoic acid

* Ber. d. chem. Gesell. 1869, 135.
† Compt. rend. 56, 222.
‡ Ann. Chem. 181, 265.
§ Ber. d. chem. Gesell. 1876, 1286.

are extremely interesting. We have seen that the formyl group has a tendency to substitute in phenol, the hydrogen atoms occupying in the nucleus the ortho- and para-positions towards the hydroxyl group. Reimer and Tiemann obtained from para-oxybenzoic acid orthoformyl-para-oxybenzoic acid and para-oxybenzoic aldehyde, the latter compound being formed by the substitution of the carboxyl of para-oxybenzoic acid by the formyl group. Reimer and Tiemann direct attention to the formation of aldehydes by the distillation of the calcium salts of organic acids with calcium formate, and consider this reaction as an analogous instance of the substitution of a carboxyl by the formyl group. But this reaction may be explained in a different manner, and according to which the analogy between the two instances in question disappears:

I.

$$\begin{array}{l|l} CH_3 & COOca \\ HCO & Oca \end{array}$$

II.

$$\begin{array}{l|l} CH_3.CO & Oca \\ H & COOca \end{array}$$

The reaction as expressed by II. is, I believe, the common acceptation, and is the most probable. For instance, according to I. we must suppose that the bond between two carbon atoms is broken in order that one of these atoms should be subsequently joined with a different carbon atom. To explain the formation of para-oxybenzoic aldehyde in the present instance, we may suppose that chloroform, with its tendency to enter in the para-position towards the hydroxyl group of phenol, acts on the sodium atom of the COONa group, forming at first the compound $C_6H_4\begin{cases} ONa \\ COO-CHCl_2 \end{cases}$, which is then decomposed by sodium hydrate into sodium chloride and $C_6H_4\begin{cases} ONa \\ COO-CHO. \end{cases}$ This compound, owing to the negative character of the group —COO—CHO, is unstable towards bases, they absorbing that part for which they have the greatest affinity, and which is carbonic acid, thus leaving the formyl group.

Finally, Reimer and Tiemann * found that by the action of carbon tetrachloride on an alcoholic solution of sodium hydrate and phenol a mixture of ortho- and para- oxybenzoic acids was

* Ber. d. chem. Gesell. 1877, 1285.

formed. This reaction, in forming the ortho- and para-acids by the use of sodium hydrate, shows clearly that it is not due to the previous formation of carbonic acid, since otherwise only the ortho-acid would have been obtained. The reaction may be explained in a similar manner to the chloroform-aldehyde reaction, the sodium hydrate extracting chlorhydric acid according to the equation:

$$C_6H_5ONa + CCl_4 + NaHO = C_6H_4\begin{cases}ONa\\CCl_3\end{cases} + NaCl + H_2O.$$

$$C_6H_4\begin{cases}ONa\\CCl_3\end{cases} + 4NaHO = C_6H_4\begin{cases}ONa\\COONa\end{cases} + 3NaCl + 2H_2O.$$

BUFFALO, *Nov. 8th*, 1879.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

IV.—ON THE OXIDATION OF ORTHOTOLUENESULPHAMIDE.

BY IRA REMSEN AND C. FAHLBERG.

Some years ago* in the course of an investigation on the oxidation of the sulphonic acids derived from toluene, one of us (R) attempted to convert orthotoluenesulphonic acid into orthosulphobenzoic acid. The analogous transformation in the para-series takes place very easily, both with chromic acid and permanganate of potassium. It was at that time shown that in the ortho-series chromic acid, as in other similar cases, fails to effect the desired oxidation. Attention was turned to the permanganate, but definite results were not reached, as is indicated by these words, quoted from the original paper: "It is possible that other oxidizing agents, as for instance potassium permanganate, may yield more satisfactory results. A preliminary experiment made with this salt in an alkaline solution showed that oxidation took place readily; and I shall soon commence the study of this reaction in detail."

* Amer. Jour. Sci. and Arts, v. 179, 274, 354; and Ann. der Chemie. 178, 275.

Numerous circumstances have prevented until the present the fulfilling of the promise here made. In the meantime one of the chief reasons for desiring the preparation of ortho-sulphobenzoic acid has lost much of its importance. It was at first hoped that, just as the meta- and para-acids can be converted into the corresponding phthalic acids by means of Victor Meyer's reaction, the ortho-acid might yield ortho-phthalic acid; and, as at that time no direct passage from a toluene derivative to phthalic acid was known, the importance of the hoped-for transformation will be readily recognized. Somewhat later Weith* succeeded in oxidizing orthotoluic acid by means of potassium permanganate in alkaline solution, and thus orthosulphobenzoic acid was robbed of much of the interest previously connected with its existence. We have nevertheless undertaken the investigation of the phenomena observed in connection with the oxidation of orthotoluene-sulphamide, a complete understanding of these being necessary as a foundation for the series of investigations which have been in progress for some time in the laboratory of this University. The results of the investigation proved to be more than usually interesting as the description will show.

Preparation of Orthotoluenesulphamide.

Two and a half pounds of pure toluene, boiling at 111-112°, were treated with fuming sulphuric acid until the toluene was completely dissolved. By means of the usual reactions the sulphonic acids thus obtained were converted into the corresponding chlorides, and these were first thoroughly washed with water at the ordinary temperature. The mixed chlorides were now brought upon an asbestus filter and the liquid drawn off as completely as possible by means of a filter-pump. Cold water was finally drawn through the solid mass on the filter until the filtrate ceased to appear oily. The liquid chloride was now separated from the wash-water and cooled down to — 15° C. Some of the solid again separated, and this was filtered off as above described. The liquid filtrate was very nearly pure orthotoluenesulphochloride. This, by treatment with ammonia, yielded an amide which after one

* Ber. d. chem. Gesell. vii, 1057.

crystallization fused at 153-154°, *i. e.*, the fusing point of pure orthotoluenesulphamide. The amide was converted into salicylic acid by fusing it with potassium hydroxide, and not a trace of paraoxybenzoic acid was formed at the same time. An analysis was made of the amide, which gave 18.72 per cent. sulphur, while the formula requires 18.71 per cent. sulphur.

Formation of Benzoic Sulfinide.

A small portion of the amide was treated with a solution of permanganate of potassium, and, as oxidation was seen to take place readily, the process was undertaken on a larger scale. The following proportions were found to yield satisfactory results: 10 grams of the amide and 40 grams of permanganate dissolved in 1 litre of water. This mixture was heated from eight to ten hours on a water-bath. The excess of permanganate was reduced by a few drops of alcohol, and the insoluble manganese compounds filtered off. The perfectly colorless filtrate was evaporated down to about 200 c. c. and again filtered. After cooling, hydrochloric acid was added and a precipitate was formed. This was easily obtained perfectly pure by recrystallization from water. As it exhibited all the properties of a chemically pure substance, it was analyzed.

I. 0.26245 gram substance gave 0.33655 gram $BaSO_4$ = 0.0462 gram S.

II. 0.2344 gram substance gave 0.2964 gram $BaSO_4$ = 0.0407 gram S.

III. 0.206 gram substance gave 0.2651 gram $BaSO_4$ = 0.0364 gram S.

IV. 0.2493 gram substance gave 16.9 c. c. N, at 15° at 761 m. m. Barom. = 0.019807 gram N.

	Calculated.		Found.			
			I.	II.	III.	IV.
$C_7H_5O_2$ ...	137	74.86	...	...	..	...
N ...	14	7.65	...	...	...	7.94
S ...	32	17.49	17.61	17.40	17.67	...
	183	100.00				

Accordingly, the empirical formula of the product is

$C_7H_5O_3NS$, whereas the formula of the sulphamine acid, the formation of which was looked for, is, $C_7H_7O_4NS$, or $C_6H_4\begin{cases}SO_2NH_2\\CO_2H\end{cases}$. The calculated percentages of sulphur and nitrogen in the latter substance are 15.92 per cent. sulphur and 6.97 per cent. nitrogen. Instead then of obtaining the normal sulphamine acid, as in the case of the corresponding para-compound, we obtained a product which differs from the sulphamine acid in that it contains a molecule of water less. It is a sort of anhydride, or a condensation-product, in which the groups CO and SO_2NH are probably connected as represented in this formula: $C_6H_4\begin{cases}CO\\SO_2NH\end{cases}$, which is certainly the simplest that can be suggested.

Similar condensation-products are known in considerable numbers, and they are almost entirely confined to the ortho-series, though a few examples are known which indicate the possibility of their formation in the isomeric series. The kind of grouping represented in the above formula is, to a certain extent, the characteristic feature of some of the compounds allied to indigo. In these we have, in all probability, a carboxyl and an amido group united as in our new product, but there are some differences in the conditions which are suggestive. In isatine, for instance, we have the group $\begin{matrix}—CO.CO\\|\\—NH\end{matrix}$ taking the place of two hydrogen atoms in the benzene nucleus, whereas in the new product under consideration the complex group $\begin{matrix}—CO\\|\\—SO_2.NH\end{matrix}$ plays a similar part. It is well known that the groups CO_2H and NH_2 can exist in the ortho-position with reference to each other in the benzene nucleus, ortho-amidobenzoic acid $C_6H_4\begin{cases}CO_2H\\NH_2\end{cases}$ being a stable compound. If, however, either the carboxyl group be removed from direct connection with the nucleus, as in the case of isatine through the intervention of the group CO, or the amido group be similarly removed, as in the case of our product through the intervention of the group SO_2, then the peculiar condensation takes place. Whatever the character of the influence may be

which is exerted upon the groups directly connected with the benzene nucleus, and which prevents the formation of the condensation-product from orthoamidobenzoic acid, it is thus seen that this influence is not conveyed through the groups CO and SO_2.

In our first notice concerning this investigation* the name *anhydroorthosulphaminebenzoic acid* was proposed for the condensation product. The only serious objection to this name is its length. As other similar products have since been discovered in this laboratory, it seems now desirable to devise a shorter generic name for this class of compounds. The characteristic feature of these compounds is the presence in them of the group $\begin{matrix}-CO\\|\\-SO_2NH\end{matrix}$. We propose to designate all compounds which contain this group as *sulfinides*, and, as they always correspond to some carboxyl derivative, to use the name of the latter to specify the particular sulfinide to be defined. Thus, the compound with which we are now concerned corresponds to, or is, in a certain sense, a derivative of benzoic acid. Hence its full name would, according to this principle of nomenclature, be *benzoic sulfinide*. A compound bearing the same relation to toluic acid can be imagined. Its formula would be $C_6H_3\begin{matrix}CO\\SO_2NH\\CH_3\end{matrix}$, and its name toluic sulfinide. Compounds of a similar nature bearing the same relation to isophthalic and terephthalic acids have actually been prepared. These may be called isophthalic and terephthalic sulfinide.

Benzoic sulfinide (or anhydrosulfaminebenzoic acid) is difficultly soluble in cold water. It is much more soluble in hot water, and can be obtained in crystallized form from its aqueous solution. It crystallizes in short thick prismatic forms, which are not well developed. Alcohol and ether dissolve it very easily. It fuses at 220° (uncorr.), but undergoes at the same time partial decomposition. It possesses *a very marked sweet taste, being much sweeter than cane-sugar.* The taste is perfectly pure. The minutest quantity of the substance, a bit of its powder scarcely visible, if placed upon the tip of the tongue, causes a sensation of pleasant sweet-

* Ber. d. chem. Gesell. xii. 469.

ness throughout the entire cavity of the mouth. As stated above, the substance is soluble to only a slight extent in cold water, but if a few drops of the cold aqueous solution be placed in an ordinary goblet full of water, the latter then tastes like the sweetest syrup. Its presence can hence easily be detected in the dilutest solutions by the taste. Orthonitrobenzoic acid has this same property, but the sweetness is by no means as intense as in the case of benzoic sulfinide.

Fused with potassium hydroxide, benzoic sulfinide is converted completely into pure salicylic acid. The reaction is a perfect one, the salicylic acid being obtained immediately in pure condition.

Phosphorus pentachloride does not act upon benzoic sulfinide either at the ordinary temperature or when heated. These facts indicate, of course, that the substance contains, as represented in the formula, no hydroxyl. Attempts were made to prepare the ethyl ester by passing dry hydrochloric acid gas into the alcoholic solution, but mostly without success. In nearly every case the unchanged sulfinide was obtained in undiminished quantity. It was found, however, that the sulfinide is more difficultly soluble in alcohol containing hydrochloric acid than in pure alcohol, for, after hydrochloric acid was conducted for some time into the dilute alcoholic solution, the original substance separated in crystalline form. This separation was not due to evaporation of the alcohol, as was determined by separate experiments.

In aqueous solution benzoic sulfinide has the properties of an acid. By neutralizing the solution with various carbonates corresponding salts were obtained, and these had the composition of salts of sulphaminebenzoic acid, $C_6H_4\begin{cases}CO_2H\\SO_2NH_2\end{cases}$. Strong acids throw down from solutions of these salts benzoic sulfinide, and not sulphaminebenzoic acid. We have not succeeded in obtaining the acid itself in free condition, and it hence appears probable that it is not capable of existence.

Barium Orthosulphaminebenzoate,

$\left(C_6H_4\begin{cases}SO_2NH_2\\CO_2\end{cases}\right)_2Ba + 4\frac{1}{2}H_2O$, was prepared by treating the aqueous solution of benzoic sulfinide with barium carbonate.

It is easily soluble in cold and hot water, but crystallizes from a concentrated solution in lustrous needles, concentrically arranged. By long standing in contact with the air it effloresces, and contains then only 9.02 per cent. or three molecules of water. It is soluble with difficulty in alcohol. It was analyzed with the results here given:

I. 0.2571 gram substance lost at 170° 0.0331 gram H_2O = 12.87 per cent. H_2O.

II. 0.2455 gram substance gave 0.094 gram = 0.0552 gram Ba = 22.51 per cent. Ba.

		Calculated.		Found.	
				I.	II.
$(C_7H_6O_4SN)_2$	...	400	64.72	...	...
Ba	...	137	22.17	22.51	...
$4\frac{1}{2}H_2O$	...	81	13.11	...	12.87
		618	100.00		

Magnesium Orthosulphaminebenzoate,

$\left(C_6H_4\begin{matrix}CO_2\\SO_2NH_2\end{matrix}\right)_2Mg + 6\frac{1}{2}H_2O$, prepared like the barium salt, crystallizes from concentrated solutions in long, transparent, hard needles. It is easily soluble in water. It crystallizes from its solution in ordinary alcohol (94 per cent.) with the same quantity of water of crystallization as it does from water. It is more difficultly soluble in alcohol than in water, and can best be obtained pure by crystallization from alcohol.

I. 0.1646 gram of the salt, crystallized from after being dried by lying in the air, lost 0.03525 gram H_2O at 180° = 12.41 per cent. H_2O, and gave 0.0396 gram $MgSO_4$ = 4.81 per cent. Mg.

II. 0.196 gram substance, crystallized from alcohol, lost 0.0425 gram H_2O = 21.68 per cent. H_2O, and gave 0.0475 gram $MgSO_4$ = 4.70 per cent. Mg.

		Calculated.		Found.	
				I.	II.
$(C_7H_6O_4SN)_2$	...	400	73.94	...	...
Mg	...	24	4.44	4.81	4.70
$6\frac{1}{2}H_2O$	...	117	21.62	21.41	21.68
		541	100.00		

Lead orthosulphaminebenzoate forms a syrupy mass which even after long standing does not solidify.

The *potassium, sodium* and *ammonium salts* are very easily soluble in hot and cold water and alcohol. They crystallize in needles from very concentrated aqueous and alcoholic solutions.

The salts of the heavy metals, as far as they were examined, do not crystallize well. All the salts prepared by us have the sweet taste which is characteristic of the acid itself. The effect upon the organs of taste is instantaneous in the case of the magnesium and barium salts which are more easily soluble than the sulfinide itself. In the case of the sulfinide, which is difficultly soluble, an appreciable amount of time intervenes between the application to the tongue and the sensation of sweetness.

As stated above, it was found difficult to prepare the ethyl ester from the sulfinide by treating the alcoholic solution with hydrochloric acid. When very strong alcohol and perfectly dry hydrochloric acid are used, an oily substance is formed which can be precipitated by water from the alcoholic solution. This, though it was not analyzed, we take to be the ethyl ester. It is soluble in boiling water and separates as an oil on cooling. It has the sweet taste characteristic of the sulfinide.

Orthosulphobenzoic Acid.

When the filtrate from benzoic sulfinide, precipitated directly after the completion of the oxidation, is further evaporated to about 75 c. c. and then allowed to stand, a potassium salt is deposited in well-formed crystals. This was separated by recrystallization from a little potassium chloride which was at first deposited with it, and was then perfectly pure. The separation from the sulfinide is very simple in consequence of the great difference in solubility of the two substances. The separation from potassium chloride requires two or three recrystallizations. The qualitative analysis of the salt showed that it contained potassium but *no nitrogen;* and, further, that the salt still possessed acid properties, indicating that it is derived from a polybasic acid. The quantitative analyses gave these results:

I. 0.2700 gram salt gave 0.097 gram K_2SO_4 = 0.0435 gram K.

II. 0.236 gram salt gave 0.2365 gram $BaSO_4$ = 0.03248 gram S.

The salt contains no water of crystallization.

		Calculated.		Found.	
$C_7H_5O_5$	...	169	70.39	...	...
K	...	39.1	16.28	16.13	...
S	...	32	13.33	...	13.75
		240.1	100.00		

The figures obtained correspond to those required by the formula of *mono-potassium sulphobenzoate*, $C_6H_4{}^{SO_3K}_{CO_2H}$. It was shown that the salt belongs to the ortho-series by fusing it with potassium hydroxide. The only product was salicylic acid, and the yield in this was quantitative. The absence of nitrogen, the acid properties, the results of the analyses and the formation of salicylic acid prove conclusively the nature of the salt.

Mono-potassium orthosulphobenzoate, $C_6H_4{}^{SO_3K}_{CO_2H}$, is precipitated in crystalline form from a concentrated solution of the neutral salt on the addition of hydrochloric acid. Recrystallized from water, it is deposited in beautiful, large, transparent plates, which appear to be monoclinic.

Dr. J. R. McD. Irby had the kindness to examine the salt crystallographically, and we are indebted to him for the following statement of his results:

"System rhombic, a : b : c = 1.4688 : 1 : 1.8129.

Forms $\{001\}$ $\{111\}$ $\{101\}$.

001 V 111 = * 65° 29⅔′ mean of 9 values from 65° 22′ to 38′.

111 V $1\bar{1}1$ = * 97° 33′ mean of 5 values from 97° 27′ to 42′.

	Calculated.	Observed.
101 V 001 =	50° 59½′	51° 3′ mean.
111 V $\bar{1}11$ =	61° 44½′	61° 43′ mean.

"Form of crystals, thin rhombic plates with edges bevelled by $\{111\}$. $\{101\}$ occasionally terminates the macro-edge of $\{111\}$. A perfect cleavage is parallel to $\{001\}$."

Orthosulphobenzoic acid is by no means a secondary product in the oxidation of orthotoluenesulphamide. From 10

grams of the amide there were obtained 5 grams of the sulfinide (dried after the first precipitation and then weighed before recrystallization) and 4 grams of the acid potassium salt. As, however, the salt is much more easily soluble in water than the sulfinide, and hence cannot be as thoroughly separated from its solutions, it seems fair to conclude that the two products of oxidation are formed in about equal quantities, probably in quantities which are proportional to their molecular weights. In other words, from two molecules of orthotoluenesulphamide there are probably formed one molecule of benzoic sulfinide and one molecule of orthosulphobenzoic acid. Both bodies are present in the oxidizing liquid in the form of potassium salts. On the addition of hydrochloric acid benzoic sulfinide is thrown down, while the neutral potassium salt of orthosulphobenzoic acid is converted into the acid salt. The question as to what becomes of the nitrogen which leaves the amide cannot be positively answered as yet. It was shown that ammonia is not formed. If we assume that it passes off in the form of free nitrogen, the oxidation may be expressed by this equation:

I. $4\underbrace{\left(C_6H_4\begin{cases}CH_3\\SO_2NH_2\end{cases}\right)}_{\text{Orthotoluenesulphamide.}}+15O+6KOH=2\underbrace{\left(C_6H_4\begin{cases}CO_2K\\SO_2NH_2\end{cases}\right)}_{\text{Potassium orthosulphamine-benzoate.}}$

$+2\underbrace{\left(C_6H_4\begin{cases}CO_2K\\SO_3K\end{cases}\right)}_{\text{Potassium orthosulpho-benzoate.}}+2N+11H_2O.$

Then on the addition of hydrochloric acid these changes occur:

II. $C_6H_4\begin{cases}CO_2K\\SO_2NH_2\end{cases}+C_6H_4\begin{cases}CO_2K\\SO_3K\end{cases}+2HCl=\underbrace{C_6H_4\begin{cases}CO\\SO_2NH\end{cases}}_{\text{Benzoic Sulfinide.}}$

$+\underbrace{C_6H_4\begin{cases}CO_2H\\SO_3K\end{cases}}_{\text{Mono-potassium orthosulphobenzoate.}}+2KCl+H_2O.$

In order to determine whether orthosulphobenzoic acid is formed as a direct product of the oxidation process, or indirectly by the action of hydrochloric acid on the potassium salt of sulphaminebenzoic acid, a small quantity of the latter was evaporated on the water-bath with hydrochloric acid. It remained completely unchanged. Further, instead of evaporating at once the liquid from the manganese precipitate after the oxidation, hydrochloric acid was first added and the liquid then evaporated. The result was exactly the same as

in the case first studied and described, so that we are forced to conclude that orthosulphobenzoic is in reality a product of oxidation of the sulphamide.

The formation of sulphobenzoic acid by oxidation of toluenesulphamide is analogous to the formation of sulphoisophthalic acid in the oxidation of sulphaminemetatoluic acid.* In both cases the sulphamine-group is converted into the sulpho-group, while, at the same time, a methyl-group in the ortho-position in the original compound is converted into carboxyl. In both cases, too, under certain circumstances, two products are formed, one containing nitrogen, the other containing none.

When benzoic sulfinide is heated in a sealed tube to 150° with concentrated hydrochloric acid, it is converted by a perfectly clean reaction into orthosulphobenzoic acid. We did not succeed in replacing the sulpho-group by hydrogen. Parasulphaminebenzoic acid conducts itself in the same way. Pure parasulphobenzoic acid was obtained and recognized through its characteristic acid barium salt. The latter was analyzed and gave 23.31 per cent. Ba, the formula, $\left(C_6H_4\begin{smallmatrix}CO_2H\\SO_3\end{smallmatrix}\right)_2Ba + 3H_2O$, requiring 23.10 per cent. Ba.

Orthosulphobenzoic acid, $C_6H_4\begin{smallmatrix}CO_2H\\SO_3H\end{smallmatrix}$, crystallizes from very concentrated aqueous solutions in beautiful, large plates which resemble in appearance the acid potassium salt above described. It fuses at 240°, at the same time undergoing decomposition. The acid is not deliquescent and can be kept in the air without undergoing change. It is very easily soluble in cold as well as hot water. Alcohol dissolves it only in small quantity, ether not at all.

Acid Barium Orthosulphobenzoate,

$\left(C_6H_4\begin{smallmatrix}CO_2H\\SO_3\end{smallmatrix}\right)_2Ba + 2\frac{1}{2}H_2O$, was obtained from the easily soluble neutral salt by adding hydrochloric acid. It crystallizes in needles which resemble those of the corresponding salt of parasulphobenzoic acid, but it is much more easily soluble in water than the para-salt. Like the latter, as well

* This Journal, 1, p. 121.

as the meta-salt, it does not give up all its water of crystallization below 200°. It is partially decomposed at 250°. The analysis gave these results:

0.287 gram air-dried salt lost 0.0238 gram H_2O at 200°, and gave 0.1155 gram $BaSO_4$ = 0.0679 gram Ba.

		Calculated.		Found.
$(C_7H_5O_3S)_2$	...	402	68.84	...
Ba	...	137	23.46	23.66
$2\frac{1}{2}H_2O$	...	45	7.70	8.28
		584	100.00	

For the purpose of comparison the *acid potassium salt* was prepared from pure orthosulphobenzoic acid. It was found to be identical in every respect with the salt described above and obtained by direct oxidation from toluenesulphamide.

Just as benzoic sulfinide can be easily transformed into orthosulphobenzoic acid, so the reverse process is also a simple one. It is only necessary to treat the neutral potassium salt of orthosulphobenzoic acid with phosphorus pentachloride, which in all probability gives rise to the formation of the normal chloride. When the chloride is treated with strong aqueous ammonia complete solution follows and, even after long standing, nothing separates. If the solution be evaporated to a small volume, the inorganic salts begin to crystallize out first. If, however, the solution be treated with hydrochloric acid, benzoic sulfinide is precipitated.

The explanation of these reactions is probably this. When the chloride is treated with ammonia, it is converted into the ammonium salt of orthosulphaminebenzoic acid, instead of into the normal amide. The addition of hydrochloric acid then causes the precipitation of benzoic sulfinide, as it does from the solution of any other salt of the sulphamine acid. The formation of the ammonium salt from the chloride may be represented thus:

$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases} + 4NH_3 + H_2O = C_6H_4\begin{cases}CO_2NH_4\\SO_2NH_2\end{cases} + 2NH_4Cl.$$

This transformation of an orthobibasic acid into the corresponding *imide* compound by successive treatment with phosphorus pentachloride, ammonia and hydrochloric acid suggests

the possibility of transforming other bibasic acids of the ortho-series in the same way. At the suggestion of one of us (R), Mr. Kuhara has undertaken the study of this reaction in connection with phthalic acid, and has already succeeded in converting phthalic acid into a beautifully crystallized substance, the analyses of which indicate that it is the imide, $C_6H_4\begin{matrix}CO\\CO\end{matrix}\!\!>\!NH$. Its properties, however, are quite different from those ascribed to phthalimide by Laurent. Other acids will be taken up in due time.

Finally, an attempt was made to convert orthosulphobenzoic acid into phthalic acid by means of the reaction with sodium formate. Equal parts of the formate and potassium orthosulphobenzoate were heated together carefully according to the directions of V. Meyer. The mass was dissolved in water and decolorized with animal charcoal. On being treated with hydrochloric acid it became turbid. It was repeatedly shaken with ether, and the ether evaporated from the extract. When the mass was dissolved in a little hot water and the solution cooled a crystalline substance separated. This was, however, not phthalic acid, for it did not fuse until a very high temperature was reached, and then it underwent decomposition and gave off, among other things, sulphuretted hydrogen. In all probability the body is similar to the one obtained by Ador in the preparation of isophthalic acid from metasulphobenzoic acid. The product was not examined further, as the quantity in our posession was very small.*

January, 1880.

ON AN UNUSUAL CASE OF ELECTROLYSIS.

By J. W. Mallet.

A galvanic battery of six couples, of Smee's construction, the flat rectangular plates about 15 by 7 centimeters, was frequently used, in connection with an induction coil, for

*Dr. Fahlberg is engaged in the study of certain other phenomena similar to those described in this paper. He will soon communicate his results to this Journal for publication.

lecture-table purposes. When not required in action the plates, all attached to the same wooden frame, were raised from the divided stoneware trough by cords wound upon an axle, and kept suspended above the acid by means of a ratchet-wheel and pawl. The two terminal copper wires were generally coiled loosely together, so as to be out of the way, when the battery was thus set aside.

On one occasion the apparatus was carried from the lecture-table to an adjoining room, the plates having been raised out of the acid, and it remained unnoticed for two or three days, when I perceived that the pawl had slipped from its place and the plates had fallen down and were fully immersed in the acid liquid — originally consisting of about one part, by weight, of sulphuric acid to seven or eight of water, but to which some additional strong acid had afterwards been added by pouring directly into the cells when, during a lecture, the action was found insufficient, the apparatus having been used at intervals for some time. This additional acid was not accurately weighed or measured, but was poured in, as far as could roughly be guessed by the eye, in equal quantity into each cell. On emptying the trough and washing off the plates, those of zinc were found much corroded, and it was noticed that one of the sheets of thin platinized silver-foil lying between them was quite stiff and very considerably thickened. Detaching it from the rest — it belonged to the third cell from one end or fourth from the other — I found that the surface on both sides was thickly coated with metallic zinc. By immersing it in pure dilute sulphuric acid in a beaker 14.813 grm. of zinc was removed, and then, the solution taking place slowly, connection was made with the negative pole of a small galvanic battery, and an insoluble opposite electrode from the positive pole immersed in the same beaker of acid, when 15.762 grm. more was removed; so that, the silver foil being now clean, 30.575 grammes altogether of zinc had been taken from its surface.

Obviously the condition of the liquid had not been quite the same in all the divisions of the trough, the acid having been of different strength; doubtless, as the plates lay neglected in it, it had first become completely converted into zinc sulphate in this particular cell, in which subsequently, the circuit being

closed by the loose contact of the terminal wires, the chemical action of the battery had transferred itself from hydrogen sulphate to zinc sulphate, this becoming a "decomposing cell," and metallic zinc was electrolytically thrown down from the strong solution of its salt.

Although the explanation of the fact is simple enough, its actual occurrence is new to me. Such an accident may have often been observed, very probably by telegraph-operators or electro-platers, but, if so, I have never seen any notice of it. It seems therefore worth a passing mention.

UNIVERSITY OF VIRGINIA, *Jan.* 24, 1880.

REVIEWS AND REPORTS.

BRIEF REVIEW OF THE MOST IMPORTANT CHANGES IN THE INDUSTRIAL APPLICATIONS OF CHEMISTRY WITHIN THE LAST FEW YEARS.

(Continued from page 361.)

MINOR CHEMICAL MANUFACTURES.

Inorganic Chemicals.

Iodine.—The chief event in the recent history of iodine production has been the utilization of the mother-liquors from which Chilian sodium nitrate has been crystallized. Cupric sulphate and sodium sulphite being added to the liquid, cuprous iodide is precipitated, and this, for the most part shipped to Europe, is afterwards decomposed by sulphuretted hydrogen or by zinc, and converted into an alkaline iodide; to a less extent the solutions are treated with a regulated quantity of sodium sulphite alone, and the iodine collected as such either by precipitation or distillation. Kelp has until lately remained the most important source of supply, although this material is worked at a serious disadvantage since its potassium and sodium salts have had to bear in the market the competition of the products of Stassfurt industry and the greatly extended Leblanc process. Large loss of iodine is known to occur in burning to kelp the sea-weeds exposed to atmospheric oxygen,

but the attempt to remedy this by charring in close vessels instead of burning, utilizing afterwards the volatile products, seems to have failed of success from the unwieldy mass of crude sea-weed requiring transportation to the seat of such manufacture. The rapid increase of demand, and consequently of price, for iodine, caused by its extensive use in making sundry of the coal-tar colors, notably the violets and greens, has been followed by a partial falling off, due to the efforts to substitute in this application other salts for the iodides of the alcohol radicles. The problem of finding means, physical or chemical, for obtaining directly from sea-water the minute amount of iodine it contains seems still perhaps worthy of consideration.

Potassium Iodide.—The medicinal use of this salt continually increases the scale upon which its production is required, while the statistics of photography show a still more rapid increase of the demand for it wherever civilized man is to be found. A recent paper by E. Schering discusses the different methods employed for making it, of which on the whole that which seems most generally in use is the solution of iodine in aqueous potassium hydrate, evaporation to dryness with addition of charcoal powder, and ignition to destroy the iodate formed; Schering himself, however, giving the preference to the production of iron iodide and decomposition by potassium carbonate.

Bromine.—It is but a short time since this was but a rare laboratory chemical; now it is manufactured by tens, nay hundreds of thousands of pounds annually, and its production upon a still larger scale is prevented merely by the low price which it commands at present. Formerly obtained only from the "bittern" of sea-water evaporation, and in a very small way from kelp, the two new sources of supply which have proved so much more extensively available are the mother-liquors obtained at Stassfurt in working the salts of potassium and magnesium, and those produced in salt-boiling in Ohio, West Virginia and Pennsylvania. One can hardly believe that new and important uses will not yet be found for this potent reagent, now mainly devoted to the production of potassium bromide, the employment of which in medicine upon a very large scale is the result of but a few years experience. The substitution of bromine for iodine alcoholic compounds in the manufacture of the coal-tar dyes was at one time eagerly attempted, then pronounced unsatisfactory, but has again, in modified form, come to some extent into use, while bromine derivatives of the hydrocarbons and phenols have played some part in the development of other branches of the industry of artificial dye-stuffs, especially of late in the production of eosine and other resorcine derivatives. It seems really desirable that a careful test shall be made of the

economy with which bromine may be substituted for chlorine in the application of Plattner's process, simplified, to saving gold from the "tailings" and "beach-sands" of the Pacific States. It does not appear impossible that such an application might be combined with arrangements for recovering at least the greater part of the bromine, but even without this, there are probably localities at which the method might be profitably used.

There is little new in the comparatively simple processes by which bromine is at present made. Some ingenuity has been shown, however, in devising the means for avoiding danger and annoyance in the transportation of so active and volatile a substance; for example, it has been shipped, when not at once made into potassium bromide, as bromide of iron, and of ethyl, in harmless solid and liquid form.

Phosphorus—In view of the small reason for making at the present day any special mystery of this manufacture, it is a little remarkable how difficult it is to obtain accurate information as to its details; probably the chief cause of this is the concentration of the manufacture in the hands of a very few firms. It is said that mineral phosphates, the so-called coprolites, Redonda guano, &c., have largely, if not for the most part, replaced bone-ash as the crude material used. It is reported, too, that instead of limiting the action upon this of sulphuric acid to the removal of two-thirds only of the calcium, all is removed as calcium sulphate, and syrupy phosphoric acid, dried up with charcoal powder, constitutes the material submitted to distillation. The suggestion made long ago by Wœhler, to dispense altogether with the use of sulphuric acid, and procure phosphorus by distilling a mixture of calcium phosphate, silica and carbon, is said to have been adopted upon an industrial scale some years since in France, but whether successfully and persistently may be doubted — the very high temperature necessary for fairly complete decomposition of the phosphate is a serious drawback. The failure of amorphous phosphorus to replace the ordinary variety in the manufacture of all friction matches has not arrested the production of the former on the large scale. In making matches the much more ready inflammability of common phosphorus causes it to be most extensively employed, but use is made of the amorphous form of the element to some extent for matches, and for the surfaces upon which "safety matches" are ignited, as well as under circumstances which make its more manageable chemical activity advantageous, as in making the haloid compounds of ethyl and methyl for the production of the aniline dyes. A new field for the use of phosphorus in metallurgy has been opened up by the introduction of phosphor-bronze, already referred to in this report.

Carbon disulphide.— This substance, possessing special value

as a solvent, has been an article of manufacture in a large way for but a moderate number of years. The scale upon which it is made has rapidly increased, but has been hardly kept pace with by improvement in the method used and in economy of result. Iron retorts have been substituted for those of clay formerly in use, and the practice has been introduced of distilling over the sulphur and bringing it into the retort in the form of vapor to act upon the red-hot carbon. The iron of the retorts is attacked and gradually converted into sulphide; although the walls are made thick enough to last for a considerable time, it seems likely that additional durability might be gained by washing over the inside surface with a moderately fusible glaze, as of borax and clay. The product is refined with much greater care than formerly, so that much of that to be found in commerce is almost quite free from the very nauseous odor belonging to the crude liquid first condensed. A large amount of free sulphur being carried over with the sulphide, having afterwards to be separated in the refining process, it would seem well to transmit the mixed vapors from the first retort through a second, or even a third, cylinder of glowing carbon before carrying them off to the condensing apparatus.

Used at first almost solely by the manufacturers of india-rubber, carbon disulphide has acquired greatly increased importance as furnishing the means of dissolving out fats and oils from various materials which could not be treated, or could not be treated with equal advantage, in any other way. Thus from oil-seed cakes, from the marc of olive oil pressing, from woolen rags and waste, from cotton waste used in wiping machinery and packing stuffing-boxes and axles, and from bones from which gelatine and phosphates are afterwards to be made, large quantities of fat are recovered. To a limited extent the same solvent has been brought into use to collect sulphur from poor "sulphur-stone," and to extract delicate perfumes and the aromatic ingredients of spices and condiments. For all these purposes a rival has appeared in the shape of the more volatile portions of petroleum, forming the so-called petroleum spirit or petroleum naphtha. The abundant supply of this at a very cheap rate has tended for a few years past to check the extension of the carbon disulphide manufacture. A new and special use for the latter has, however, quite lately grown up in its application as such, as well as of the *sulpho-carbonates*, as the means of checking the ravages of the *phylloxera* in European, especially French, vineyards. Later the ethyl- and amyl-disulphocarbonates have come into use for this purpose.

Potassium amyl-disulphocarbonate is said to have proved cheapest and most easily prepared by simply bringing together, with precautions against too great rise of temperature,

a strong solution of potassium hydrate, amyl alcohol of fusel oil, and carbon disulphide.

Arsenic acid — has come to be largely manufactured to be used in the conversion of commercial aniline oil into fuchsine, common arsenious oxide being treated with boiling nitric acid, or dissolved in hot hydrochloric acid and submitted to the action of a stream of gaseous chlorine. The recovery and utilization of the arsenic from the residues of fuchsine production has been attempted in various ways, none of them quite satisfactory on both economic and sanitary grounds. Sodium arseniate constitutes a large portion of the "dung substitute" used by calico-printers in developing sharp, well-defined patterns with clear grounds, and has come to be made on a pretty large scale by treating arsenious oxide with strong soda-lye, evaporating and fusing the residue with sodium nitrate.

Oxygen gas.— The nearest approach to a process fit for successful technical use in making gaseous oxygen upon a large scale is undoubtedly that of Tessié du Motay, consisting in exposing sodium manganate at a low red heat to a current of superheated steam, reproducing the manganate from the residue of manganese sesqui-oxide and sodium hydrate by passing purified air over it at the same temperature. The cost of the gas is still far from having been reduced to the point at which it might be, with great advantage, used for many industrial purposes, notably in the manufacture of sulphuric acid in closed chambers; but the gas may be said to have acquired a certain commercial foothold, and its application in some directions has been facilitated by the system of storing it under a pressure of several atmospheres in portable iron cylinders. In giving control of a temperature at which platinum and iridium may be melted into large ingots, in affording the means of producing light of an intensity comparable with that more commonly now derived from an electric current, and under conditions sometimes more conveniently available than the latter, and in its medicinal application the gas has already rendered useful service. Under this last head the notices in some scientific works and reports of late years have tended to give an unduly depreciated idea of the therapeutic value of the substance. While the old notion of the respiration of pure oxygen having any *chemical* value is of course no longer entertained, the relief which may be afforded a patient in the advanced stages of phthisis, in pneumonia and any other affection interfering in a purely mechanical way with the volume of air with which the lungs can be effectively supplied, if once witnessed, will not be underrated or denied.

The preparation and sale, in similar compressed form, of nitrogen monoxide for dentists' use, and of hydrogen for employment with oxygen in the production of the "calcium

light," have become common, though upon no very great scale. For making hydrogen industrially the plan of Tessié du Motay is worth notice — namely, heating surplus carbon with slaked lime, giving rise to the reaction $Ca(HO)_2 + H_2O + C = CaCO_3 + 2H_2$, and reproducing calcium hydrate by passing steam over the heated carbonate which has been formed. Save for a few special purposes, as occasionally for filling balloons so as to give them unusual ascensive power, it seems unlikely that the place of pure hydrogen in industrial applications cannot be equally well or better taken by the gaseous mixture which contains it along with carbon monoxide, nitrogen, &c., known as "water gas" or "generator gas."

Many other substances might be named which have gradually been passing, under the eyes of those still of the present generation, from the domain of the scientific or the pharmaceutical laboratory into that of the manufacturing chemist. There seems no reason to doubt that *ozone* has for some time been more or less experimentally used in bleaching sugar, while hydrogen dioxide has been brought into the market as the "Eau de la Fontaine de Jouvence" for partially destroying the color of human hair, pending any serious use of it in bleaching textile fabrics. *Nitrous acid* and *nitrites* have taken rank among the regular working reagents of the maker of coal-tar colors. *Silver nitrate* is made by tons for the purposes of the photographer, as well as for medical and surgical use. The *double salts of ammonium with nickel or cobalt* are consumed in great quantity by the electro-plater, while salts of such rare metals as *vanadium* and *cerium* are regularly applied in the processes of calico-printing.

Organic Chemicals.

In the production of these much greater changes have occurred, and much greater advances have been made within but few years than has been the case in regard to inorganic materials. Most of the substances in question, however, find their application in connection with particular arts, and are better considered in relation to these. A few may be noted here.

Methyl alcohol has long been used as a solvent, but more largely than ever with the progress of manufacturing organic chemistry, and under the influence of revenue laws permitting ordinary alcohol, when mixed with this wood spirit, to be used without heavy taxation. In the coal-tar color industry, moreover, methyl alcohol itself and several of its derivatives play an important part. For the production of the methyl acid derivatives of rosaniline, &c.,

Methyl chloride has taken the place of the dangerous methyl

nitrate and to some extent of the more expensive iodide, without, however, displacing altogether the latter, and has also been brought into use as one of the materials for the production of artificial cold by rapid evaporation in closed vessels.

Ethyl alcohol up to almost "absolute" strength and well freed from foreign alcoholic and other impurities, can now be had in commerce, distilled in apparatus capable of more rapid and delicate fractional separation of the distillates than was industrially common not long ago. Amongst the more extensively prepared products from ordinary alcohol,

Ether and *chloroform* are made chiefly by processes long in use, and which have undergone no important modification of late (chloroform is made to a small extent from chloral hydrate), but greater pains are taken with the final purification, sometimes now carried out by other hands than those which have turned out the crude product, and a much higher and more uniform standard of purity has consequently been attained by the best makers for medical and surgical use.

Chloral hydrate has taken its well recognized place among therapeutic agents and become an article of regular manufacture upon a very large scale. In a much smaller way *iodoform* has also entered the field of industrial production.

Ethyl iodide and *bromide* enter largely into the resources of the coal-tar color maker, and the latter, as above noticed, has been made the means of safely transporting bromine, to be afterwards recovered in the free state, if desired, with regeneration of ordinary alcohol.

Amyl alcohol has ceased to be regarded solely as a mischievous impurity of distilled spirits, and has, with some of the compounds obtainable from it, come to find useful applications. Amylated derivatives of rosaniline and allied color bases are made from the iodide, bromide and chloride, while *amyl nitrite* and *valerianic acid*, with its salts, have become common products for medical use.

Few substances have acquired more widely extended importance than *glycerine*, both on account of its special or individual properties and those which, in modified form, it shares with bodies earlier known and used. Its history, however, rather belongs with that of the fats from which it is derived.

The manufacture of *phenol* or *carbolic acid* has developed a distinct branch of the many-sided industry of coal-tar, and in beautifully pure, colorless, crystalline form replaces the coarse, dark-brown "coal-tar creosote" which alone was known but a few years ago.

Cresol and *thymol* have also become regular articles of manufacture.

Benzoic acid is said to be still made to some extent from benzoin, or perhaps partly from Australian "acaroid resin"

(of *Xanthorrhea hastilis*), but is mainly and largely obtained by evaporating the urine of herbivorous domestic animals and boiling with hydrochloric acid to decompose the hippuric acid present. Some is also produced in France, by Poirrier and others, by continuous boiling of benzyl chloride with strong nitric acid. The conversion of naphthaline into phthalic acid, and this into benzoic, seems to have proved on the large scale less advantageous. Beside the consumption of benzoic acid in making the artifical colors for dyers' use, there is reason to believe that it enters to some extent into the composition of the secret nostrums used in flavoring manufactured tobacco.

Salicylic acid may more properly be considered in its special relations among antiseptics. Its synthetic production by Kolbe's process from phenol-sodium and carbon dioxide represents one of the most admirable gifts of pure chemistry in modern times to medical, sanitary and industrial progress.

Phthalic acid is another of the products called for by the maker of artificial chemical dye-stuffs. The use of its anhydride in the development of eosine and the other beautifully colored derivatives of Baeyer's phthaleins has led to its being itself largely made from the naphthaline which was so long associated almost solely in chemists' minds with the classical "light-bearing" researches of Laurent.

In connection with the same great field of the last twenty years' work upon the colored products obtainable from tar, innumerable chlorinated and brominated derivatives of hydrocarbons, phenols, acids have been made upon a larger or smaller scale; and of late still more extensively organo-sulphonic acids, but for the most part these have not formed the final products of separate chemical manufactures, but have constituted single steps in the work of the producers of the dye-stuffs themselves.

In regard to the treatment of *the natural vegetable alkaloids* recent times have not been without their evidences of progress. Attention has been given to improving, both in quantity and quality, the supply of original material, notably in the direction of cinchona cultivation under Dutch and English auspices in Java and Southern India, and in connection with such efforts chemistry has aided in some measure as a guide to practice. The scale upon which *quinine*, *morphine*, *strychnine* and *atropine* were formerly made has undergone very great extension, and although no radical change has probably been made in the processes by which these alkaloids are extracted, the final purification has been much improved, especially as to the more easily alterable bases, and new solvents have served to cheapen the processes and facilitate crystallization. The other cinchona alkaloids which accompany quinine have, either singly or in admixture, been brought to some extent into use instead of merely accumulating them as worthless

by-products. Some new substances of this class have been made available for medical purposes and are added to the list of those manufactured, as for example, the *eserine* of Calabar bean; while among the products of chemical alteration *apomorphine* has been found valuable. Researches of a purely scientific character upon the less known substances classed as vegetable alkaloids, but turning out to be in some cases complex mixtures, as aconitine and veratrine, promise to yield results before long of practical applicability.

Mechanical Applications of Chemical Manufactures in General.

Among the chief directions of improvement in the "plant," appliances, and physical methods of working of chemical factories may be noted:

Improved grinding mills, especially those run at comparatively high speed and aiming at true grinding rather than crushing.

The extended use of *steam coils* and *steam jackets* for heating purposes, admitting of complete control and nice regulation of temperature.

Heating by vapor from materials under treatment, such an adjustment being made of the different portions of the work as to permit of this utilization of otherwise waste heat, and sometimes allowing of simplification in the working itself.

Heating under pressure greater than that of the atmosphere, the use of so-called "autoclaves," often arranged with special ingenuity as to the details of filling, emptying, observing the progress of reactions occurring within, &c., playing an important part in some of the branches of modern chemical industry.

The use of "ice machines" for the *production of artificial cold.* These valuable machines have lent most important aid in various directions, enabling results of solidification, crystallization, rapid cooling to determinate temperatures, &c., to be secured in climates and seasons, and under temporary conditions of weather which would otherwise prove serious if not insuperable obstacles. In many cases uniformity of working is gained by the control thus given of temperature in the downward, as formerly in the upward, direction. In turn, manufacturing chemistry has been called upon to supply the materials used in most of these machines to produce cold by evaporation, as ethyl and methyl ethers, methyl chloride, petroleum spirit (mainly butane), ammonia and sulphur dioxide, the machine working with air alternately compressed and expanded alone using a material furnished by nature.

Improved mechanical arrangements for agitation or stirring of liquids, including under this head not only revolving paddle-

arms and the like contrivances, but the blowing in of air or steam, often now made to accomplish the work of stirring and mixing, and at the same time that of heating, oxidation, &c.

Extended use of *vacuum pans* for evaporation, with or without arrangements for condensing the vapor given off. The vacuum pan has long ceased to be a part only of the special plant of the sugar refinery, and has become one of the well recognized appliances of the general manufacturing chemist, without which much of the treatment of the more delicate and easily alterable materials he has to deal with could with difficulty be accomplished.

Improved apparatus for distillation, especially that intended to effect nice fractional separation of liquids differing often but little in boiling point. The extension upon a manufacturing scale of the processes of organic chemistry has given to this increased importance.

Introduction of the method of *distillation by means of, or along with super-heated steam.* In certain cases this enables a simple physical purification of special materials to be effected which otherwise would require elaborate and tedious chemical processes to be used.

The general application of "*centrifugal machines*" or "*hydro-extractors*" for draining and washing suitably divided solid materials, especially crystals. The quickness and thoroughness with which the work is done, and the limited amount of wash-water or other fluid necessary, constitute important advantages.

The use of *filters arranged to work with a partial vacuum*, so as to expedite filtration and leave the solid residue in a more effectually drained condition.

The use of *filter presses* to mechanically squeeze out the liquid tenaciously retained by precipitates, sediments, skimmings, &c. These have been much improved of late by the general substitution of metal for wood in their construction, the increased pressure obtainable—commonly up to 120 or 130 lbs. per square inch — the rapidity with which the pressure is brought to bear and the readiness with which it may be regulated, the thoroughness with which a small quantity of washing fluid may be made to remove residual soluble matter, and the substantial and durable character given to the framework and mechanism. In a multitude of cases chemical industry has derived most valuable aid from these useful pieces of mechanism in their more modern forms.

J. W. MALLET.

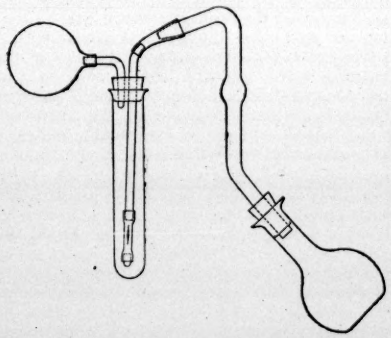
(To be continued.)

NOTES.

A New Form of Absorption-Apparatus for Use in Estimating Ammonia.

In attempting to estimate ammonia by the process which involves its expulsion from its compounds by the action of boiling solutions of caustic alkali and its collection in hydrochloric acid, it frequently happens, even when great precaution is taken to prevent it, that, on account of the difficulty of regulating the evolution of the gas, small amounts of ammonic chloride are carried with escaping air through the absorption bulbs in ordinary use, and discharged visibly from the apparatus, such loss introducing more or less inaccuracy into the determination of ammonia when it is made to depend upon the amount of ammonic chloride retained within the apparatus, whether this is weighed directly or estimated indirectly after precipitation as ammonio-platinic chloride.

The difficulty may be overcome by the use of a very simple apparatus of the following construction: Through a perforated rubber stopper fitted to the mouth of a flask having a capacity of 70 cm.^{3} or 80 cm.^{3} passes a glass tube of about 0.7 cm. interior diameter, about 20 cm. long, and bent as shown in the accompanying figure. About midway of the vertical



part, which has a length of 10 cm., the tube expands to a small bulb, and at the upper end it is joined by means of a rubber connector to a second tube, which passes through a doubly-perforated stopper fitted to the mouth of a test-tube holding about 30 cm.^{3}, and ends in a valve consisting of a piece of rubber tubing closed at the lower end with a bit of glass rod and pierced with a longitudinal slit. Through the second perforation of the stopper of the test-tube passes a tube, as shown in the figure, over whose outer end the neck of a small rubber balloon (such as are sold in the shops attached to toy-whistles) is drawn and securely fastened. The apparatus when thus put together must be air-tight.

When a determination of ammonia is to be made with the aid of this apparatus, the test-tube is filled to a point somewhat above the valve with dilute hydrochloric acid and placed in a vessel of cold water; the ammonia salt is put into the flask with a bit of platinum foil (to secure quiet ebullition), and 20 cm.^{3} or 30 cm.^{3} of a sufficiently strong solution of sodic or potassic hydrate; heat is applied to the flask and its contents rapidly boiled until the greater part of the water has been converted into steam and the ammonia completely driven over with the steam through the valve (which prevents the return of any part of the liquid in the test-tube when the pressure wavers) into the hydrochloric acid — the air which filled the apparatus in the beginning now collecting, together with that portion of the ammonic chloride which escapes detention in the acid, in the upper part of the test-tube and in the balloon, which it distends.

The action proceeds quietly and no special care is required during the operation. The flask being properly inclined, and the conducting tube of suitable size, there is no danger of a transfer of solid matter from the flask to the absorption-tube by the agency of bubbles ascending the conducting tube; for, under these conditions, bubbles rarely appear at all in the conducting tube and could never by any possibility pass the bulb.

At the end of the operation the tubes are disconnected at the rubber joint, the stopper of the test-tube loosened to permit the balloon to collapse, and the contents of the test-tube, together with the rinsings of the test-tube and its accessories — the washing of the interior wall of the balloon, upon which some small amount of ammonic chloride has fixed itself, being easily accomplished by throwing a fine stream of water into the balloon through its connecting tube and ejecting it again by pressure upon the exterior — transferred to an appropriate receptacle and treated in one or another of the usual ways.

The chief points of the device are its effectiveness, convenience and simplicity; and these qualities may render its application in other analytical processes equally anvantageous.

F. A. Gooch.

Glucose.

It is known that saccharose combines with bases giving sucrates, while glucose by treatment with alkalis yields glucic acid, which differs in composition from glucose by the elements of water, and melassic acid, which is allied to the ulmic compounds. PÉLIGOT has found the following new facts: Glucose obtained from starch or by the action of acids upon sugar combines with lime, forming unstable products which are rapidly transformed into others. Lime dissolves largely in water containing 15–20 per cent. of glucose. The solution is at first alkaline, but gradually loses its alkalinity, becomes brown and finally deposits a yellow substance, sometimes of crystalline appearance. The same precipitate, more strongly colored, is produced quickly by boiling the filtered solution. Under these circumstances there is formed glucate of lime, part of which remains in solution and can be separated by sub-acetate of lead. At the same time another substance is formed which has escaped the notice of the author and other chemists who have worked with these substances for more than forty years. Accident revealed it to the author. Resuming the somewhat neglected study of glucic acid, he found in a kind of molasses, obtained as a by-product in the preparation of the acid, fine prisms which he first mistook for glucic acid. This led to further attempts, which were successful, to get the substance in this form. These crystals have the composition of saccharose, $C_{12}H_{22}O_{11}$, but the substance is not sugar; it does not ferment with yeast, and is not sweet, but rather bitter to the taste. The author calls it *saccharine.* It is distinct from the other substances having the composition of sugar, is not easily soluble in cold water, and is in large part volatile. Nitric acid, 36° Beaumé, and concentrated sulphuric acid hardly act upon it, nor does it reduce ammonio-cupric tartrate except by long boiling. It crystallizes very readily when pure. The author is inclined to think that the sugars instead of being polyatomic alcohols are esters, and that this action with lime is a true saponification. He surmises that saccharine may prove to be an alcoholic substance.—(*Compt. rend.*, Dec. 1st, 1879.)

New Metals.

In the *Comptes rendus* for Oct. 22, 1878, Marignac announced the probable existence, in the *erbia* of Bunsen and Clève extracted from gadolinite, of a new earth, the oxide of a metal for which he suggested the name *ytterbium.* The small amount of material which he possessed prevented the complete study of the substance, but he was able to describe certain properties which he considered established its idividu-

ality. He gave provisionally the molecular weight 131. Its spectrum was studied by Soret. Nilson of Upsala then took up the subject, having larger quantities of material at his command, and was able to isolate and study chemically pure *ytterbia*. He found the molecular weight of the oxide 131.92 and 132.17. Thalén studied the substance spectroscopically in connection with Nilson, and his work tended to show the presence of still another new earth. The latter Nilson called *scandia*, and made a partial chemical examination of it, finding its molecular weight below 90, calculated for ScO.* Subsequently Clève extracted scandia from gadolinite and yttrotitanite of Norway, and studied it more fully. He found that the only oxide of scandium was Sc_2O_3, and the atomic weight of the metal 45. This was so much smaller than Nilson's number that he suspected the presence of another earth. But Thalén examined its spectrum and pronounced it pure scandia. Nilson's substance must hence have been mixed with seven or eight times its weight of ytterbia. Clève gives an extended chemical description, and shows that it corresponds almost completely, point for point, with the description given by Mendelejeff of the hypothetical metal *ekabor*, of atomic weight 44.

Soret, when studying the spectrum of ytterbia, as mentioned above, was led to suspect the presence in erbia of another new earth besides ytterbia, and designated it provisionally as X. The probable existence of such a substance had been indicated by Delafontaine and Marignac. Subsequently Delafontaine gave the name *philippia* to a substance found by him and considered identical with Soret's X. He gave a partial chemical and spectral description in *Comptes rendus*, Oct. 14th, 1878, stating provisionally the molecular weight of the oxide as 90–95. Soret admits himself unable† upon the publications of Delafontaine to affirm or deny the identity of philippia with X, but is inclined to consider them identical. He thinks the existence of X well established.

Clève has given reasons based principally upon study of spectra for supposing that erbia contains, besides ytterbia and scandia, three different earths, which he named *erbia*, *holmia* and *thulia*.‡ But Lecoq de Boisbaudran and Soret both pronounce the spectrum of holmia identical with that of X.§ Soret had also called attention, in connection with X, to the lines which Clève describes as characteristic of thulia, but he did not consider the indications of the spectra alone as sufficient evidence for the announcement of a new element. Lecoq de Boisbaudran says his own studies, not yet completed, tend to confirm the idea of Soret, Clève and Thalén.

Delafontaine has claimed the discovery of still another

* Compt. rend. March 24th, 1879.
† Ibid. Sept. 15th, 1879.
‡ Ibid. Sept. 1st, 1879.
§ Ibid. Sept. 15th, 1879.

earth in samarskite, which he calls *decipia*. He has given a description of its spectrum,* and indicated its approximate molecular weight as 122.

The same investigator, followed by Lecoq de Boisbaudran and Soret, has found in the spectrum of the earth known as didymia evidence tending to show that the substance contains at least two different earths. And Lecoq de Boisbaudran obtaining still more definite results, has proposed the name *samarin* for one of them.

Lawrence Smith announced to the French Academy, September 22d, 1877, the discovery of a new earth in samarskite, which he called *mosandra*. But Marignac and Delafontaine, who examined the substance, pronounced it identical with the *terbia* of Mosander.† September 1st, 1879, Smith states that he has not yet obtained the earth in a satisfactory state of purity, but claims that it differs from terbia. As it does not give absorption bands, he is obliged to depend upon chemical study.

July 7th, 1879, Hiortdahl announced to the same body the discovery of a new earth designated as *norvegia*, but gave no description.

On Coto Bark and its Constituents.

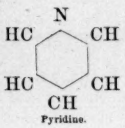
Jobst and Hesse have recently subjected the genuine coto bark from Bolivia to a careful examination, and have established a number of valuable facts concerning it. Without entering into a detailed description of their results, we may call attention to a statement made in the original paper which may prove of very great interest to the general public. The bark has the reputation in Bolivia of being an excellent remedy in cases of intestinal diseases. Dr. v. Gietl concludes, as the result of an extensive experience in the use of this material, that it is a *specific against diarrhœa in its different modifications*. Dr. Burkart has shown that the bark and the tincture cause certain objectionable after-effects if taken into the system. On the other hand, *paracotoïn*, which can be prepared from the bark, and which is described by Jobst and Hesse, is an excellent remedy. A number of cases are cited illustrating the beneficial effects of administering it in cases of chronic diarrhœa and Asiatic cholera.—(*Ann. der Chemie*, 199, 82.)

Transformation of Piperidine into Pyridine.

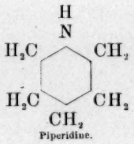
In the last number of this Journal attention was called to the fact that pyridine and its homologues have of late been the subject of a number of investigations most of which tend

* Compt. rend. Oct. 28th, 1878. † Ibid. Aug. 12th, Oct. 22d, 1878.

to show that there exists close relation between the natural alkaloids and the pyridine series. A short time ago Hofmann showed that a product can be obtained from piperidine which resembles very closely one obtained from pyridine. Though this fact indicated a close relation between pyridine and piperidine, no transformation has hitherto been effected which proves the relation. KOENIGS has now succeeded by a simple process in transforming piperidine directly into pyridine. It is only necessary to heat the former with sulphuric acid at 300° for about seven hours. The change effected is one of oxidation. It is suggested that the piperidine, $C_5H_{11}N$, bears to pyridine, C_5H_5N, the relation of an addition-product. Assuming Koerner's formula for pyridine to be correct, the relation may be expressed thus —



Pyridine.



Piperidine.

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